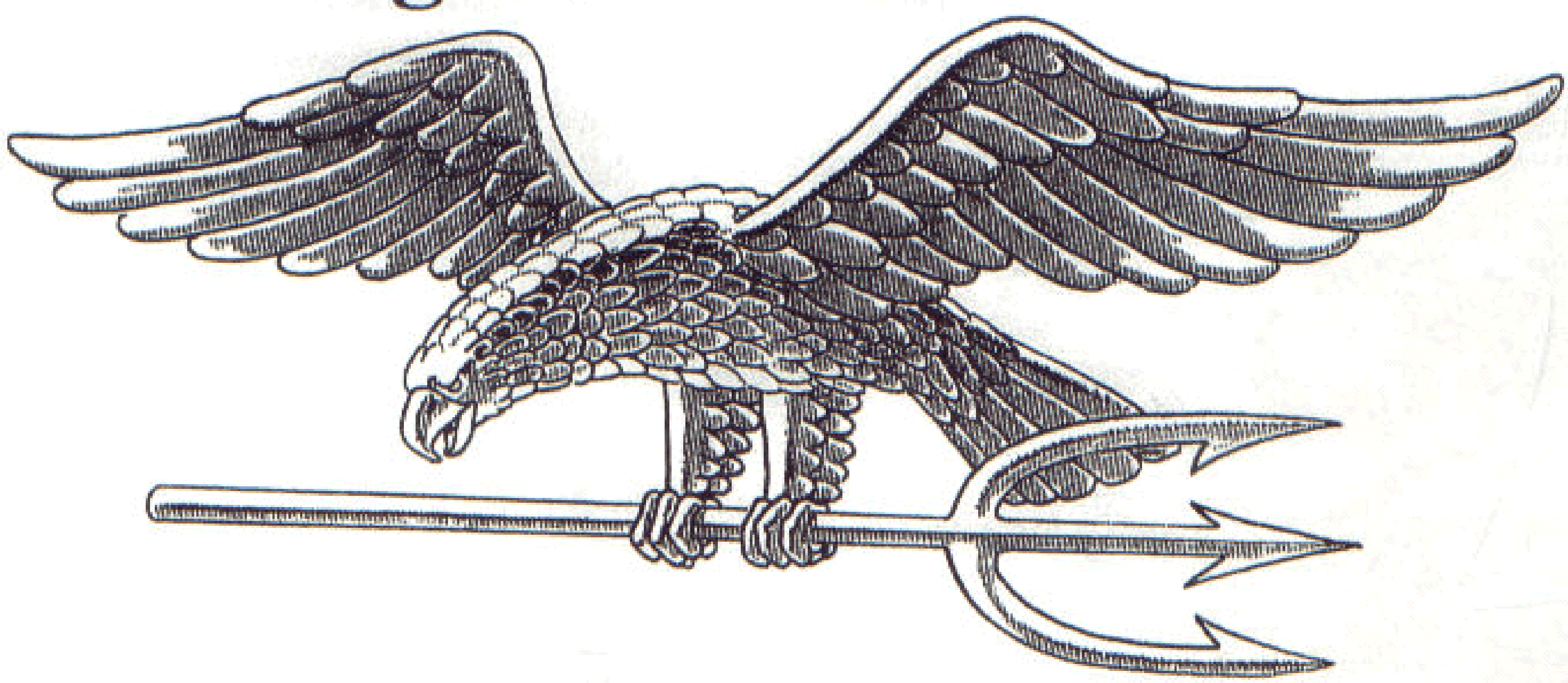
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SCIENTIFIC PRINCIPLES OF IMPROVISED WARFARE AND HOME DEFENSE
Volume 5

Advanced Chemical Weapons Design and Manufacture



Chemicals that kill in 30 seconds or less

(or your next book is free)

For Academic Purposes Only

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Warfare and Home Defense
Volume 5
Advanced Chemical Weapon Design and Manufacture

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Advanced Chemical Weapons Design and Manufacture

Chapter 1

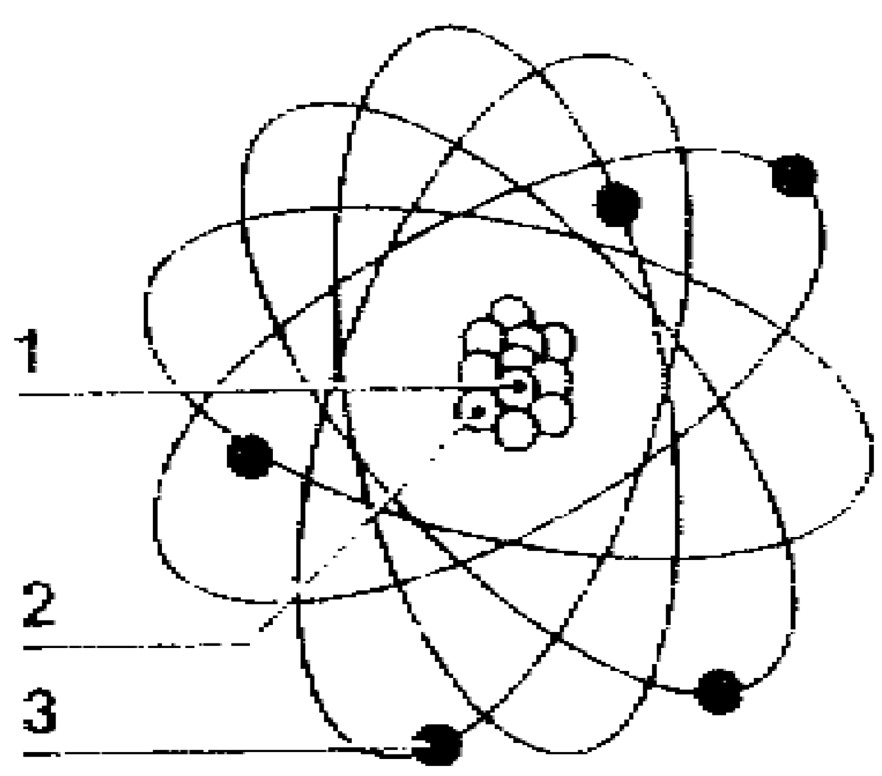
Basic Chemistry

In order to understand how chemicals cause harm thereby making them useful as weapons, a basic number of chemical ideas must be understood. I will teach a handful of these principles in this book. My objective is not to teach chemistry, but to give the reader enough of a basic understanding of how chemicals are made that they can be used in war.

All material is made up of **atoms**. These atoms are all listed in the periodical table of elements we described in Vol. 4. Here, we are going to go into more detail of what these chemicals are and how they combine to make other forms of matter called **molecules**. It is these atoms and molecules that form materials that can cause harm to humans, animals, plants, and machinery. How they cause harm will be covered in the next chapter.

Atoms are made up of small parts.

1. Protons
2. Neutrons
3. Electrons



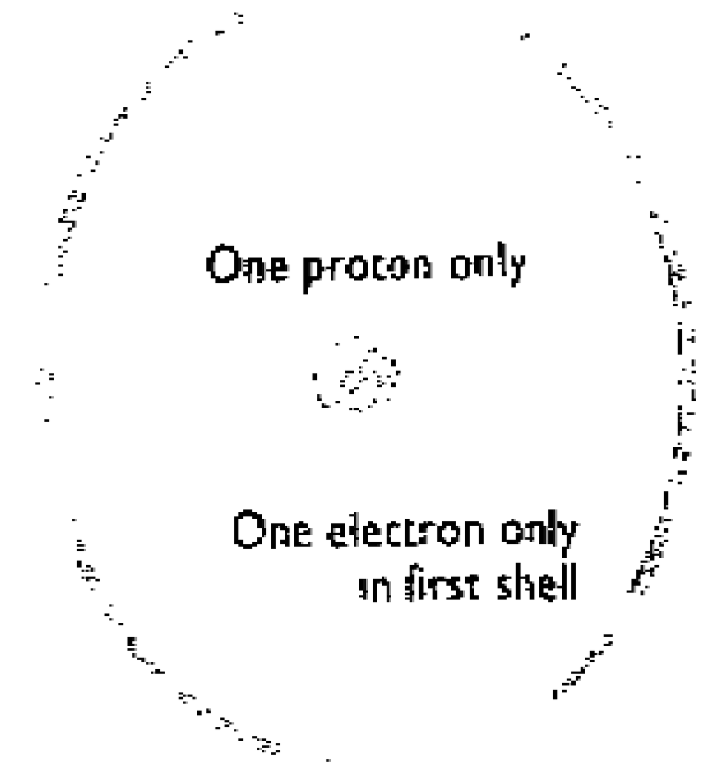
The number of **Protons** in the nucleus determines what the atom is. If it contains one proton it is called Hydrogen. If it contains two protons it is called Helium, and so on.

Neutrons also exist in the core of an atom with the protons and adds weight to the atom. When the number of neutrons is different in an atom than is "normal" for that substance, then the new substance is called an isotope of that element.

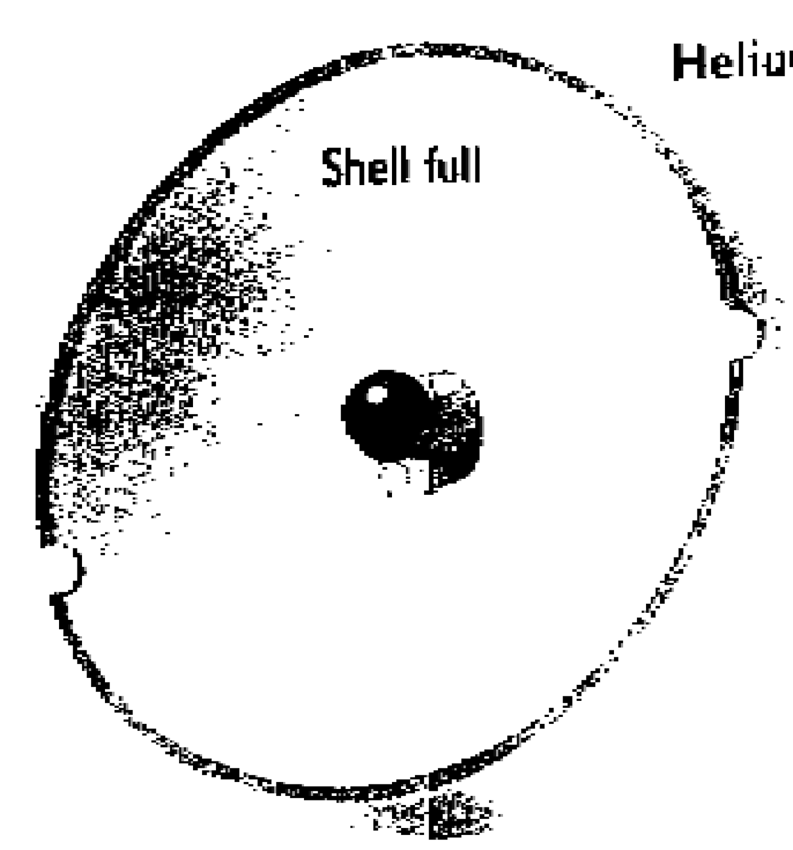
Electrons move around the center or nucleus of its protons and neutrons like the planets which orbit around the sun. These electrons move at very high speed and it is their arrangement around the atom which determines how the element will behave chemically. This arrangement will determine how the atom will combine with other atoms to form molecules. It also determines how they can be used to cause harm to living organisms or damage or destroy other materials. Understanding this is important to understand how chemicals can act as weapons so we will teach this science electron behavior here.

Protons have a positive electrical charge and the electrons have a negative electrical charge while neutrons are neutral. Most atoms have exactly the same number of electrons and protons so that they balance each other and this makes the atoms electrically neutral.

The electrons exist in what we call clouds or shells. The first cloud or shell can hold up to two electrons in orbit around the nucleus. If the nucleus contains only one proton it is the element **hydrogen**. It is normal for it to have one electron in its outer shell as pictured here. The element **helium** has two electrons in its outer shell and this number fills the outer shell. Once an outer shell is filled, the atom becomes stable. One of the rules of chemistry is that atoms will look for other atoms around them to combine with, or share atoms in the outside shell so that they will form stable molecules. Hydrogen has only one atom in its outside shell so it looks for other atoms to react and combine with. Helium has its outside shell filled so it is considered a stable or "inert" element.



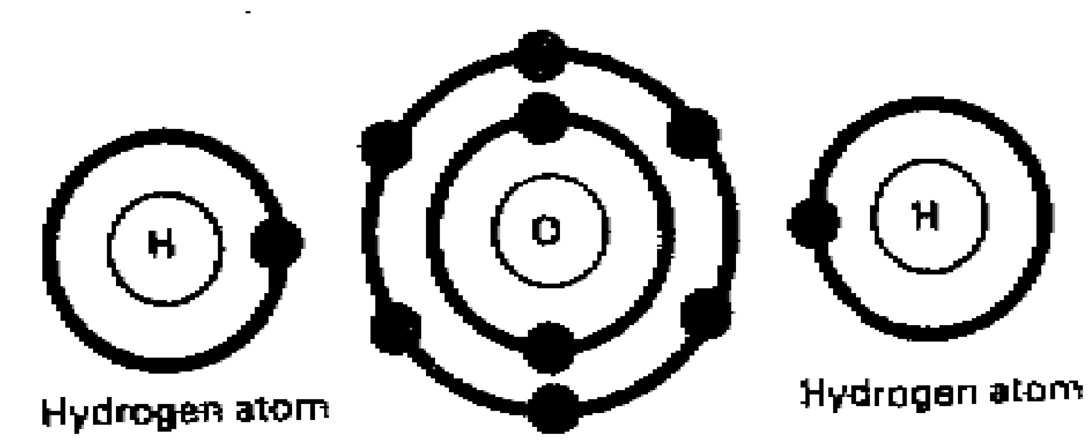
Hydrogen atom



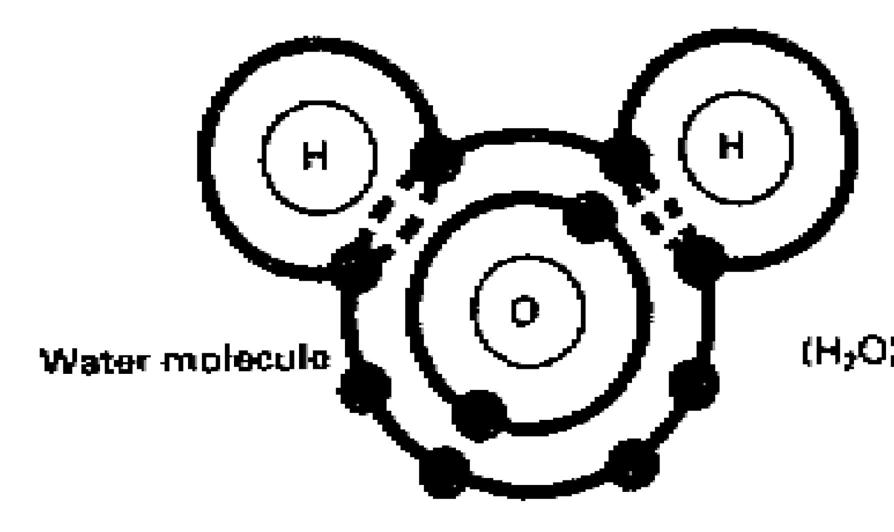
Helium atom

When hydrogen was used in airships like the "Hindenburg" blimp, it was very reactive and could catch fire easily. This is exactly what happened when the Hindenburg exploded in the 1930's. The highly reactive hydrogen gas chemically combined with oxygen in the air and this chemical reaction released the heat of the explosion that was filmed and witnessed by millions since then. Breathing hydrogen gas in large volumes cause many reactions in the lungs which results in a burning sensation. When Drano or sulfuric acid is poured into clogged sinks, they often release hydrogen gas. The feeling of having your breath taken away and the funny electrical sensation is the millions of reactions of the hydrogen directly forming new molecules with materials in your lungs. If the amount of hydrogen is great, it can cause injury or even death from these reactions.

After the first shell is filled, the electrons start on a new shell or cloud. This second shell can hold up to 8 electrons. The **Oxygen** atom has only 6 electrons in its outer shell so it will look for other atoms which can provide 2 more electrons to fill the shell.

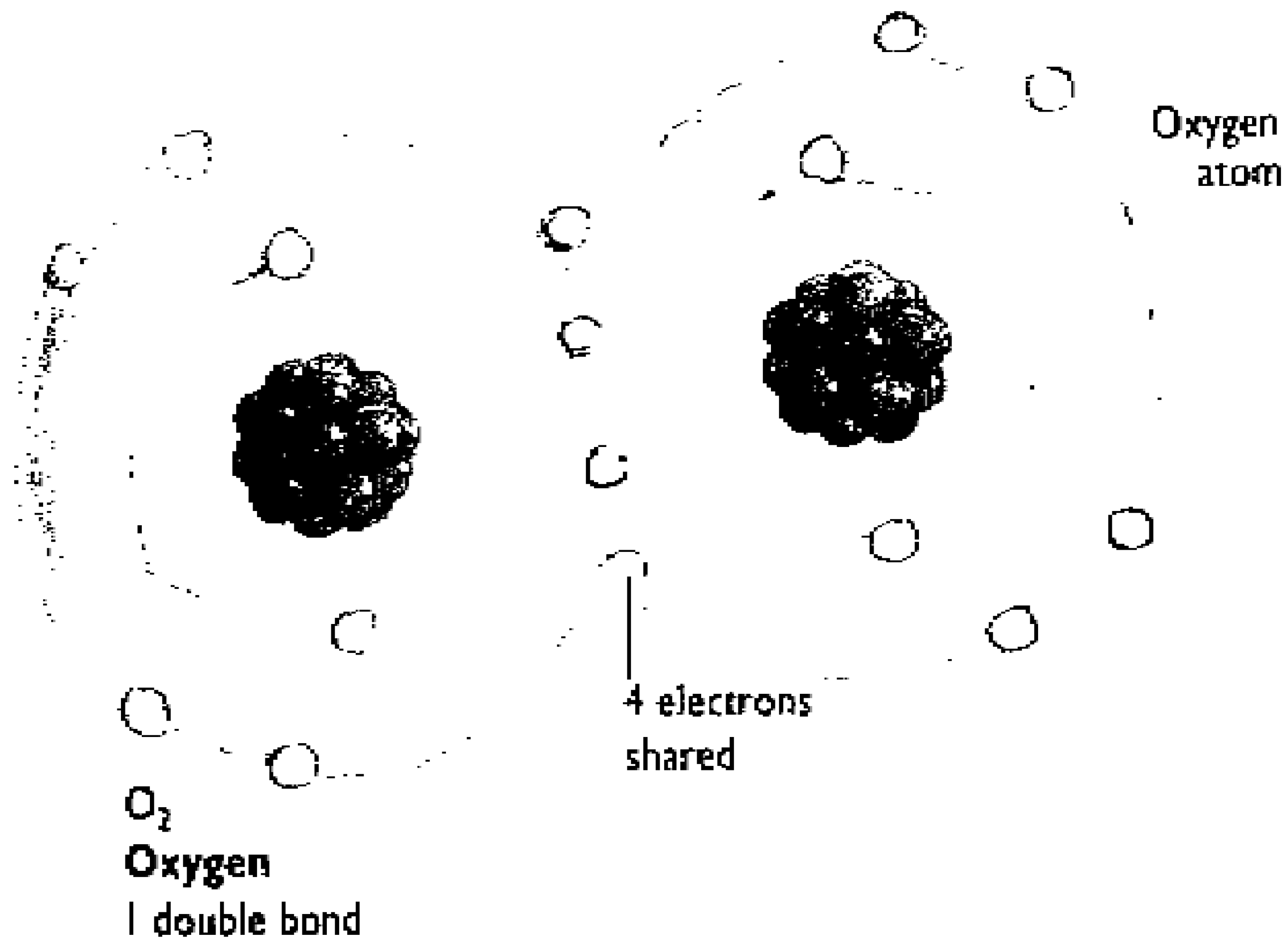


Hydrogen needs one atom to fill its outer shell so two atoms of hydrogen combine with one atom of oxygen to make a stable complete molecule of water. These electrons are shared in the outer orbits of each atom. When liquid oxygen is combined with hydrogen in rockets, the reaction produces water which is superheated in the reaction and pushes the rocket forward.



The oxygen shares 2 electrons and each of the hydrogen's shares and electron to form the stable and strong water molecule.

If hydrogen is not available, the oxygen will combine with itself and form the molecule O2. It shares two double bonds with each other. Hydrogen combines to form H2 the same way.



Now the obvious question occurs. If the outside shells of these atoms have already been filled by combining with each other then why do they break apart to form water or react with other materials. There are two more concepts which govern how atoms combine. These are -

1. Unlike electrical charges attract each other.
2. Electrons tend to exist in pairs.

These two ideas help explain how the atoms in over 10 million substances will bond to each other and why some materials attract each other (such as water wetting a glass but not wax).

The actual atomic structure of the atom (which causes it to be located in particular groups in the periodical table of the elements) is what governs how it will react with other atoms. Its structure causes it to form one of 5 major types of chemical bonds. These are -

1. **Ionic Bonding**: such as table salt (sodium chloride).

2. **Covalent Bonding**: for molecules like water, methane, sugar, and polymers.

3. **Intermolecular Bonding**-

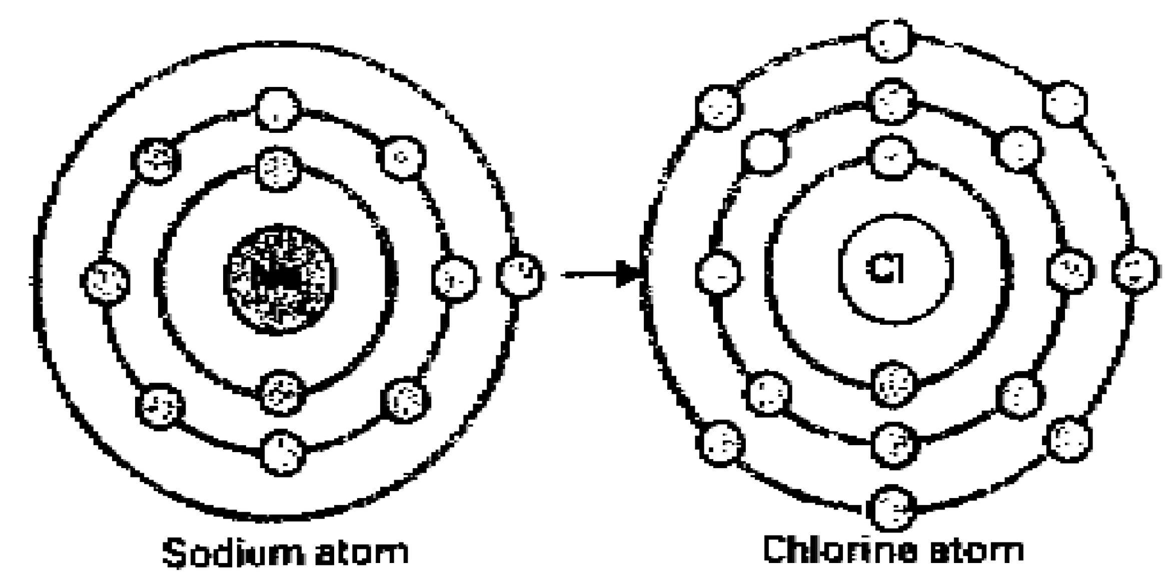
    a. **Hydrogen based** as in ammonia, DNA, and proteins

    b. **London Forces** in materials like liquid helium and solid CO2 (dry ice)

4. **Metallic Bonding**: seen in metals and alloys.

Ionic Bonding

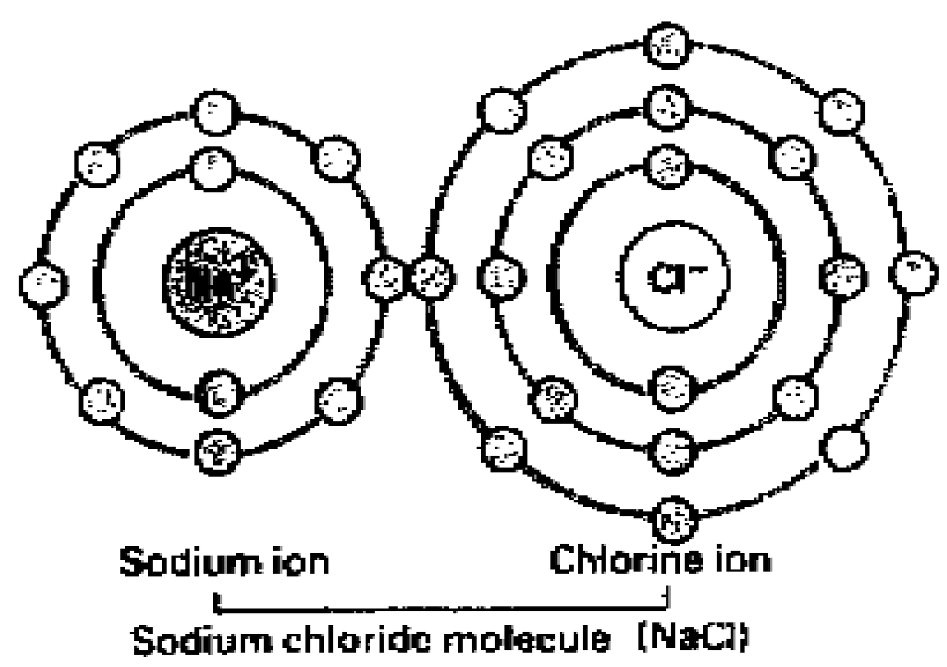
occurs most often when metals and non-metals join together by transferring electrons to form stable outside shells. This means that they do not actually share electrons in the outside shell. The atoms that easily give or take electrons to form these compounds are called -



Cations which are positively charged ions or

Anions which are negatively charged ions

The best example of this is common table salt. The elements Sodium and Chlorine combine by forming Ionic bonds. The sodium gives up its only electron in its outer shell to chlorine which is one electron short in its outer shell. The sodium now becomes a cation with a positive electrical charge and is written as Na+. The chlorine gains this electron and forms the chloride anion Cl-.



The sodium is a very reactive, solid metal while the chlorine is a very reactive, corrosive, and poisonous gas. Once they form ionic bonds, each of these elements now have full outside shells containing 8 electrons in their orbits. Both atoms now have opposite electrical charges. The sodium is positive and the chlorine is negative. Since opposite electrical charges attract each other, the two atoms are strongly attracted to each other, bond to each other, and arrange themselves into solid salt crystals when dry.

The electrostatic forces that hold together these kinds of ionic solids and are very strong. Even in liquid form the bonds are strong and as a result, these compounds have very high melting and boiling points. They usually dissolve easily in water where the bonds between the ions weaken and they separate or drift around freely in water. This is why salt can be added to an electrochemical cell in water and separated by the electric current as we taught in Vol.'s 3 and 4. This process is called electrolysis. Because the salt ions are mobile in the water and electrically charged, they also conduct the electricity very well. Batteries reverse this process by using terminals made from two different metals. Atoms are then drawn from the cathode as cations into solution which leaves an excess of electrons behind. This creates an electric charge which can be stored for later use.

Chlorine is very reactive because it takes electrons away from other elements to fill its outer shell and forms a negative electrical charge. This combination allows it to react with living tissues. As a war gas, it dissolves in the water on the skin and membranes creating hydrochloric acid which then forms strong ionic bonds through acid reactions with many tissues. These reactions destroy the living tissues while forming new salts which is what kills the target.

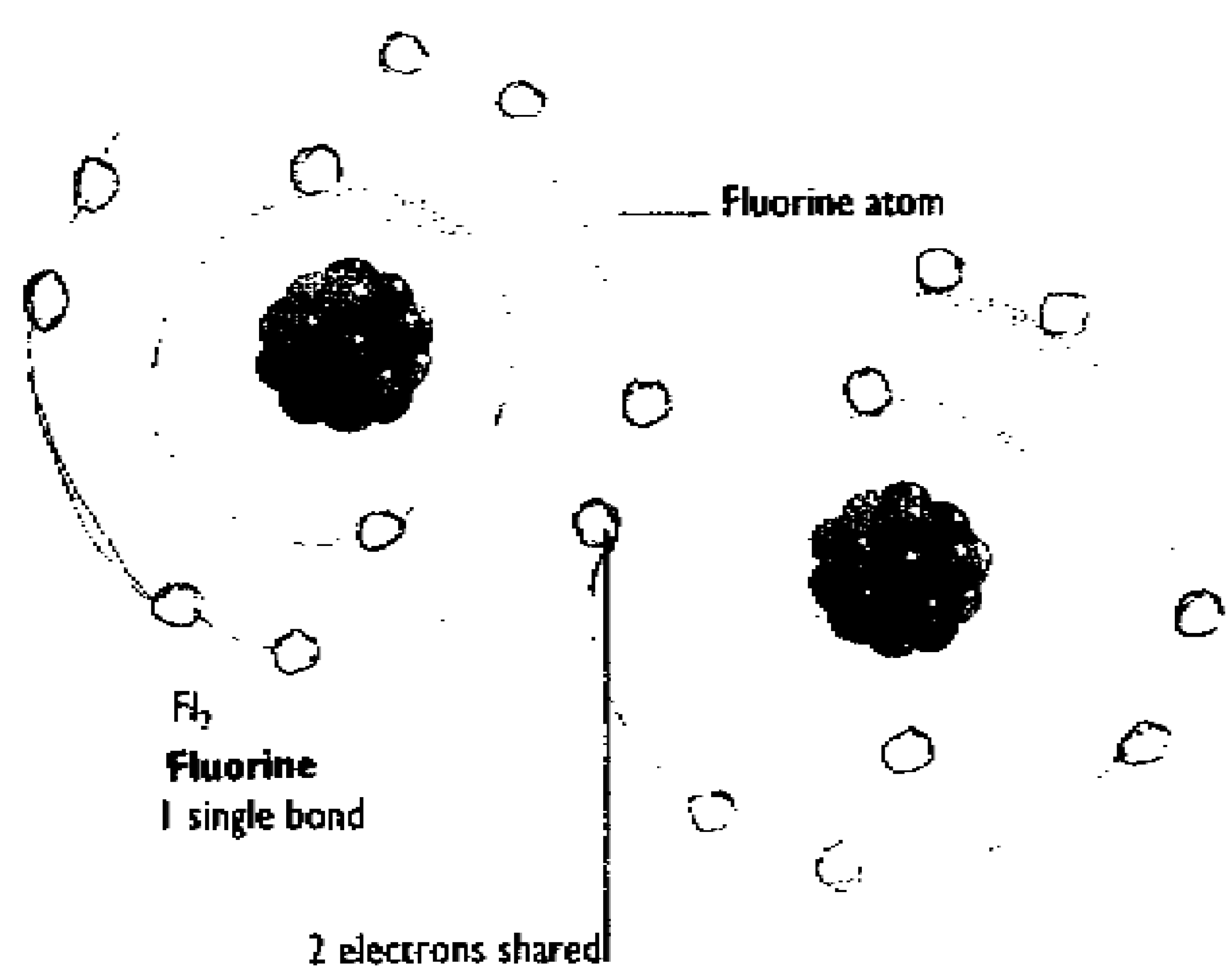
Covalent Bonding

Covalent bonding occurs when nonmetal elements react to share electrons to fill their outer shells. This is what happens when two hydrogen or oxygen atoms come together and form bonds to hold themselves together.

The theories behind what holds these types of atoms together are complex. Since most of my readers are presumed to have little or no chemistry background I will attempt to explain what happens here in layman's terms.

When the two hydrogen atoms come together, there is no electrical charge formed to hold or attract them together like you have in ionic bonding. In fact, both nucleus are actually trying to repel each other. The two hydrogen's are existing together in a state where there is some energy from this type of closeness that forces them apart so that they are barely holding onto each other.

When fluorine atoms combine, they form F2 in which they share two outside atoms as a covalent bond. What actually is taking place is that there is a powerful need to fill the outside shell. At this same time, the nucleus of the two atoms are repelling each other. Also at this same time, the other six pairs of electrons are actually repelling each other as well. This makes this molecule very reactive. If another chemical comes along that will easily form stronger bonds, it takes very little energy for the two fluorine atoms to separate and form new molecules with the other atoms.



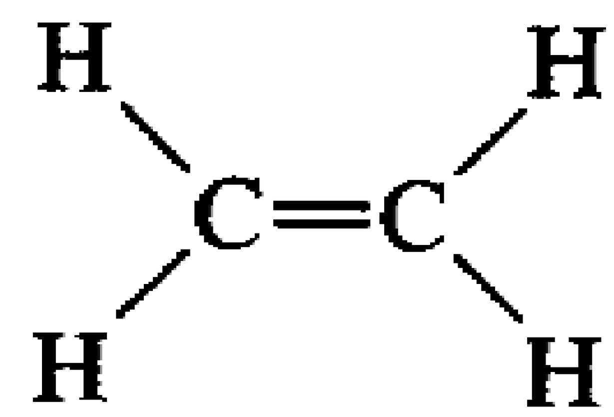
Some covalent bonds can be formed as strong and stable molecules that do not easily react with anything else. Most however have varying energy levels based on how their outside shells will fill up and react with other substances. Entire chemistry books are written on this science and it is very predictable.

A good example of the above paragraph would be Nitrogen. The atom Nitrogen forms strong covalent bonds with itself and is stable and unreactive. Fertilizer manufacturers use the chemistry of pressurizing the nitrogen in the air and combining it with hydrogen to form a more reactive and weakly bonded molecule called ammonia. While nitrogen will not break apart to supply N to plants in the ground, the more weakly bonded ammonia readily reacts with plant roots to give up its nitrogen so the plant can grow. This is also why we can breathe the nitrogen in the air without harm. Because of the weak bonds of ammonia, breathing this gas in can quickly kill us because it reacts inside our body easily in several harmful ways.

In many circumstances, atoms can form more than one covalent bond with each other. A good example of this is carbon dioxide in which carbon forms two double bonds each with oxygen.

O= C=O

When three pairs of bonds are involved they are called triple bonds. Molecules can contain many types of bonds. The molecule ethylene can be shown here using lines to represent the bonds. One line stands for single bonds and two lines for triple bonds.



The bonds that form between atoms follow some general rules.

1. Triple bonds are shorter than double bonds which are shorter than single bonds.
2. As bond length decreases, bond energy increases. This is because the orbits interact more intimately.
3. Bond energy is the amount of energy needed to break the bonds of the molecule.

The following chart compares bonds of nitrogen and carbon atoms. As you can see, the more bonds holding the atoms together, the harder it is to break them apart.

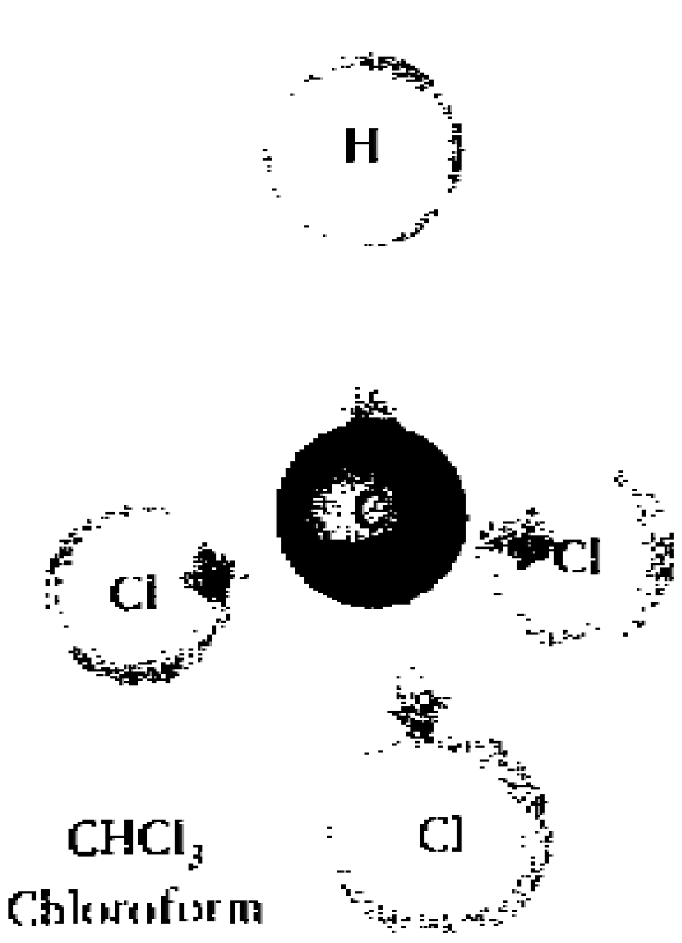
Bond type	C—C	C=C	C≡C	N—N	N=N	N≡N
Bond length (nm)	0.154	0.134	0.120	0.140	0.124	0.109
Bond energy (kcal/mol)	83	146	200	40	100	225

kcal/mol (kilocalories per mole) = thousands of calories necessary to break 6.02×10^{23} bonds.

When atoms forming a molecule are the same, like the two hydrogen, oxygen or fluorine pairs we have shown, there is an equal sharing of the electrons. When two atoms are sharing a bonded electron and are not the same element, there is a shift in electric charge toward one of the pairs. The relative power of attracting electrons by an element is called its electronegativity. The more powerful this electronegativity, the more powerful the attraction on the electrons. Also, the more nonmetallic the element is the more it attracts electrons. Fluorine is the most electronegative of the elements.

When two atoms of different electronegativity are bonded covalently, they are said to have formed a **Polar** covalent bond.

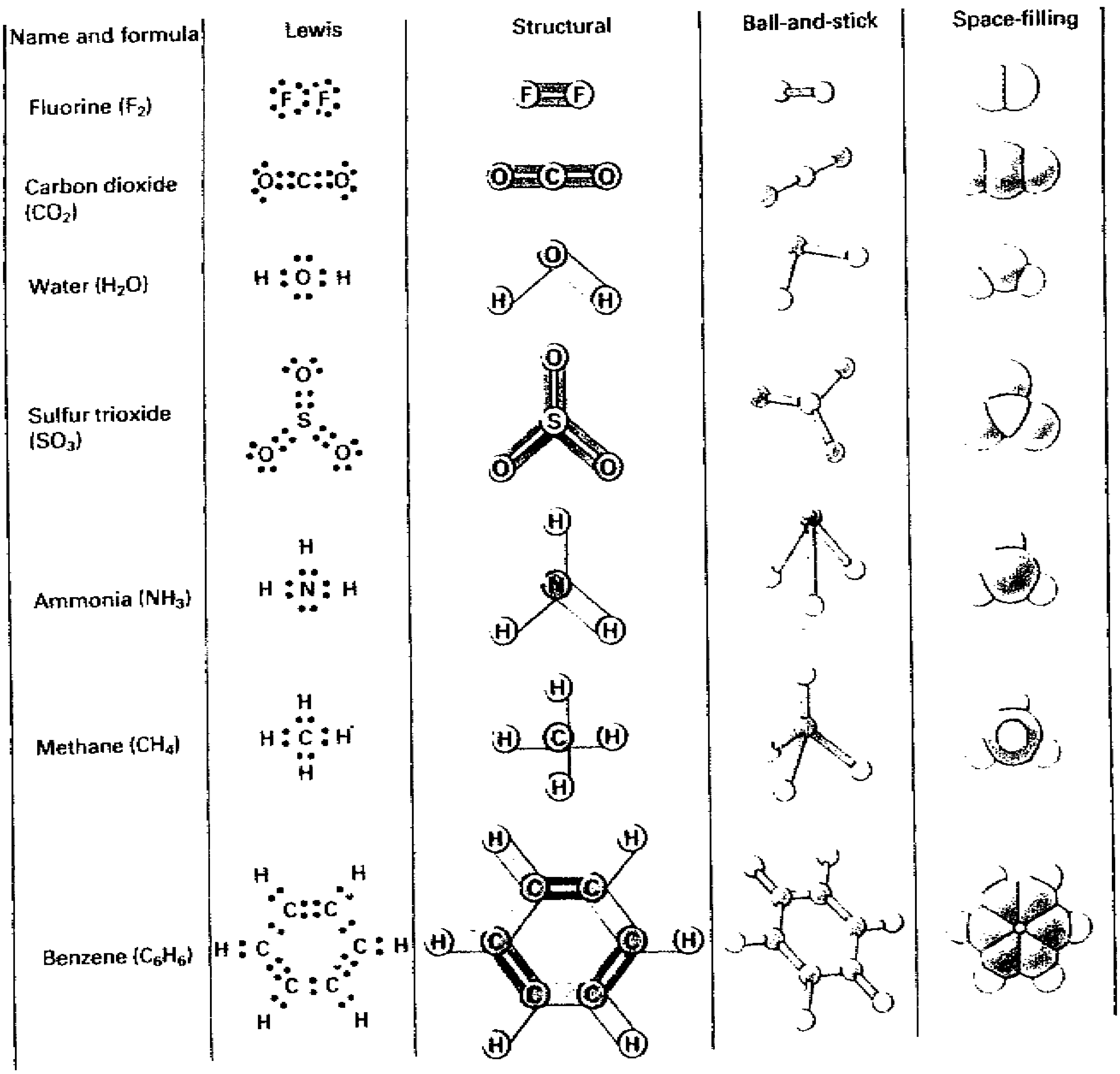
Chloroform
Polar Bonds
Strongest with Chlorine, less with Hydrogen.



$CHCl_3$
Chloroform

As we have shown on the last page, there are many ways that atoms and molecules can be represented. The following chart shows several ways of visually representing chemicals.

The "Lewis" system shows the electrons in the outer shells of the atoms as dots.
The "Structural" shows the letters and their connections.
The "Ball and Stick" shows the atoms as balls and the bonds as sticks.
The "Space Filling" shows the elements in relative size and in different colors.



Hydrogen Based Intermolecular Bonding

When covalent bonds are formed between a hydrogen atom and a highly electronegative element like fluorine, oxygen, or nitrogen (F,O,N), conditions occur that allow an intermolecular positive to negative attraction to occur that is called hydrogen bonding. This bond is produced by the attraction between the slightly positive hydrogen atom and very electronegative F,O, or N.

What happens is that an electron pair shifts towards the F,O,N atom and causes the atoms to take on a partial negative charge. The hydrogen bond becomes a bridge between two highly electronegative atoms and is now bonded both covalently and electrostatically. These types of hydrogen bonds are responsible for things like hard candy getting sticky, lanolin being able to soften skin, the shapes of proteins and enzymes, and many odd behaviors in water.

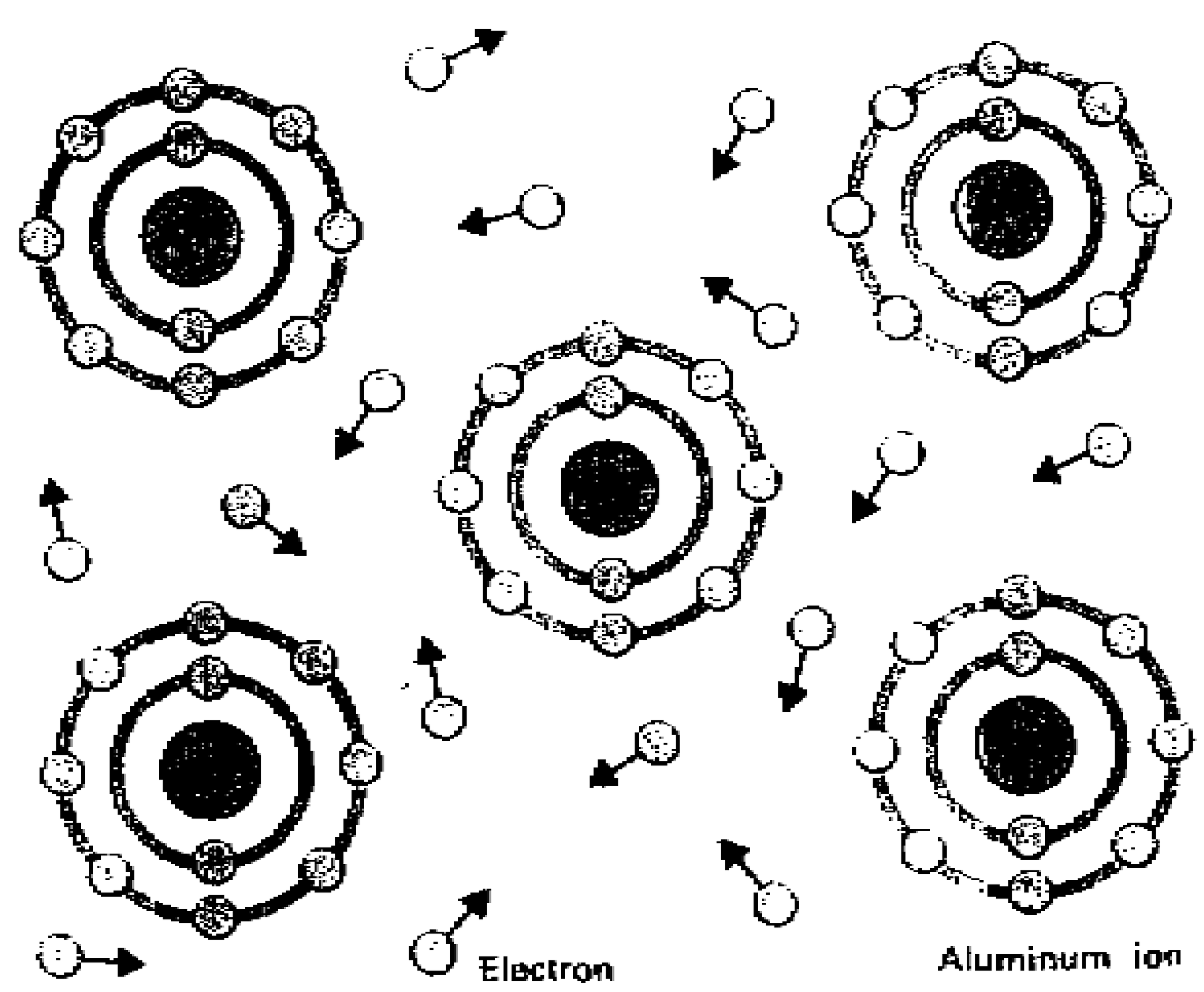
Hydrogen bonds also cause the boiling points of molecules to be higher than normally expected. This is also why water does not turn to a gas and boil at room temperature like other gases that do not contain a high electronegative element. The best examples are Methane (CH_4) and Ammonia (NH_3). This property of hydrogen bonding also affects the properties of military war gases as we will see in later chapters.

London Forces

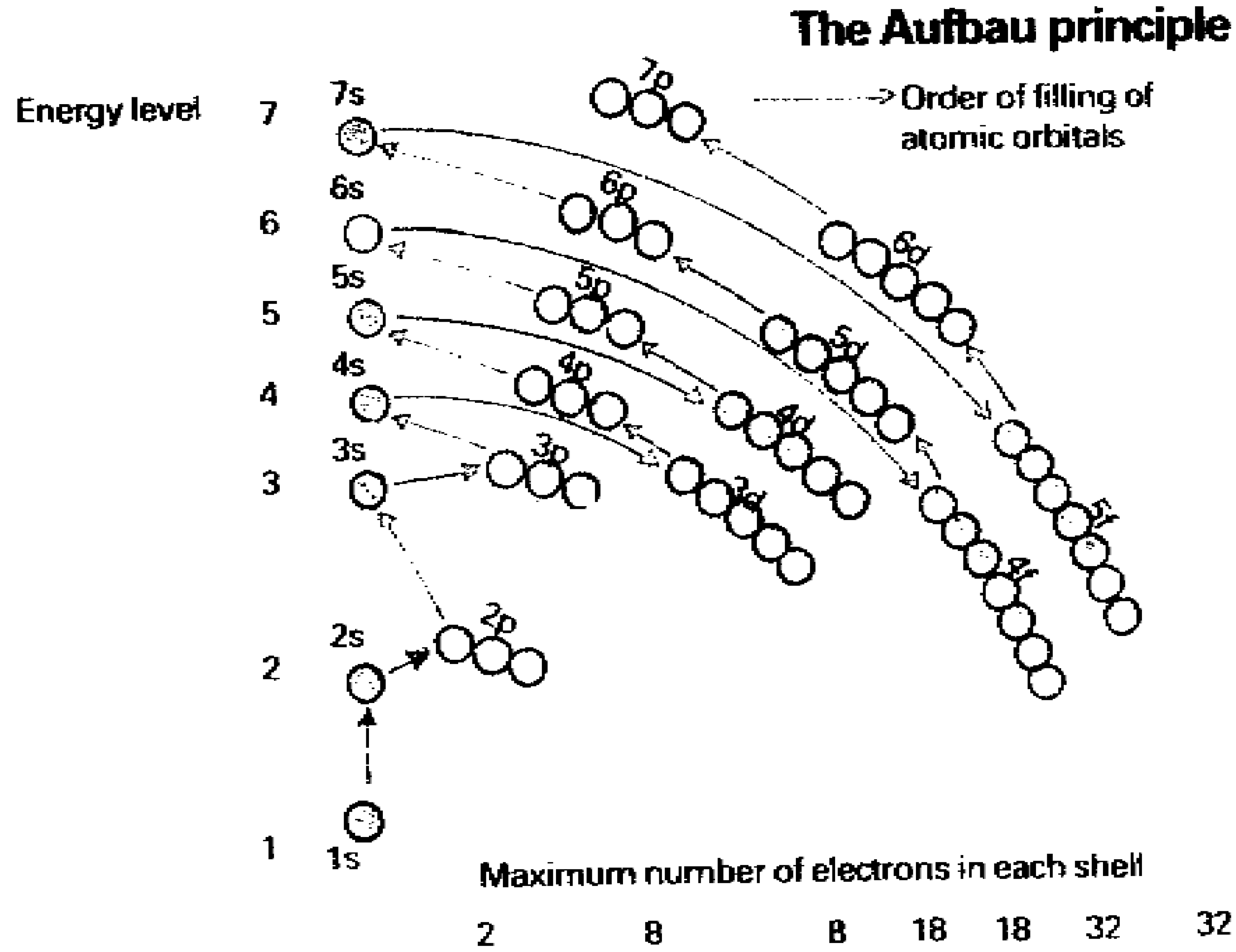
There is a weak attraction called "London Forces" that causes a shifting in the electron clouds of some atoms. These atoms are usually the same and form polar bonds with each other because of a "dipole" electrical effect. This effect allows some gases like O_2, He_2, and N_2 to exist as solids at very low temperatures.

Metallic Bonding

There are over 80 kinds of metals, over 4/5ths of all the elements. They have unique properties of being able to form bonds by providing electrons from their outer shells to a common pool. This sea of electrons that are "free" allow metals to conduct electricity and heat, makes them easily beaten into new shapes, or drawn into wires without breaking. Mixing metals with other elements produces new properties which is why a little carbon can be added to Iron to make steel.

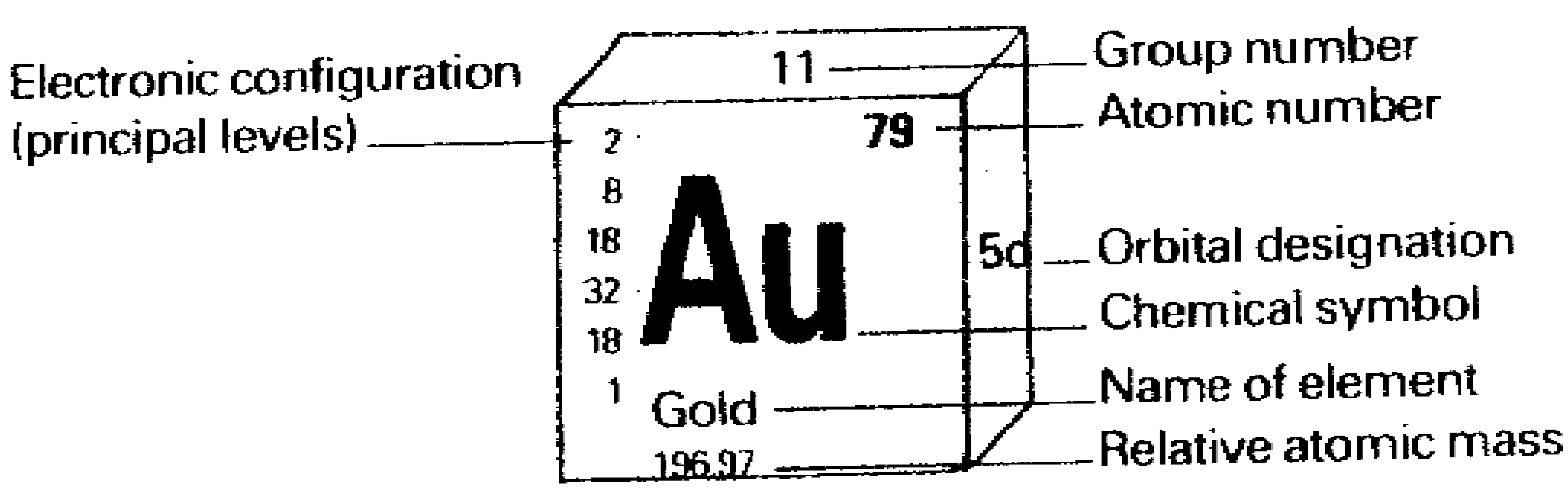


A final concept of the electrons around the nucleus of atoms involve the "Aufbau" principle. This is a chart which describes the shells that exist for all the elements and the normal order in which they are filled. At energy level 1 there is a shell called the 1s which contains a maximum of 2 electrons. At energy level 2, the shell is called 2s with a second shell in the same level called 2p. When 2s fills up, the electrons start filling 2p and so on for each level.



The **Periodical table of Elements** (which we showed you in Vol. 4) is broken into parts.

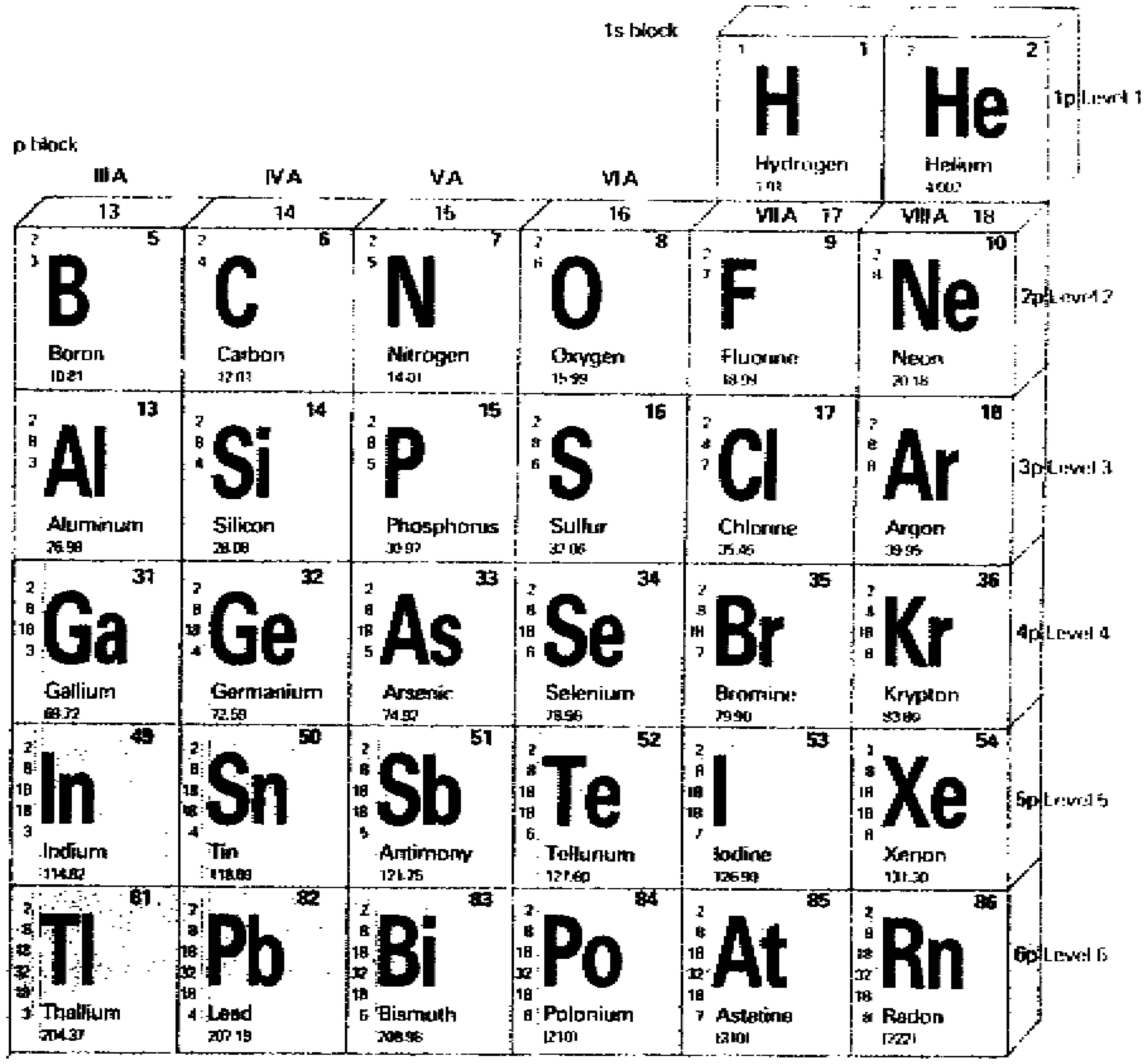
Each element contains the following information in its block.

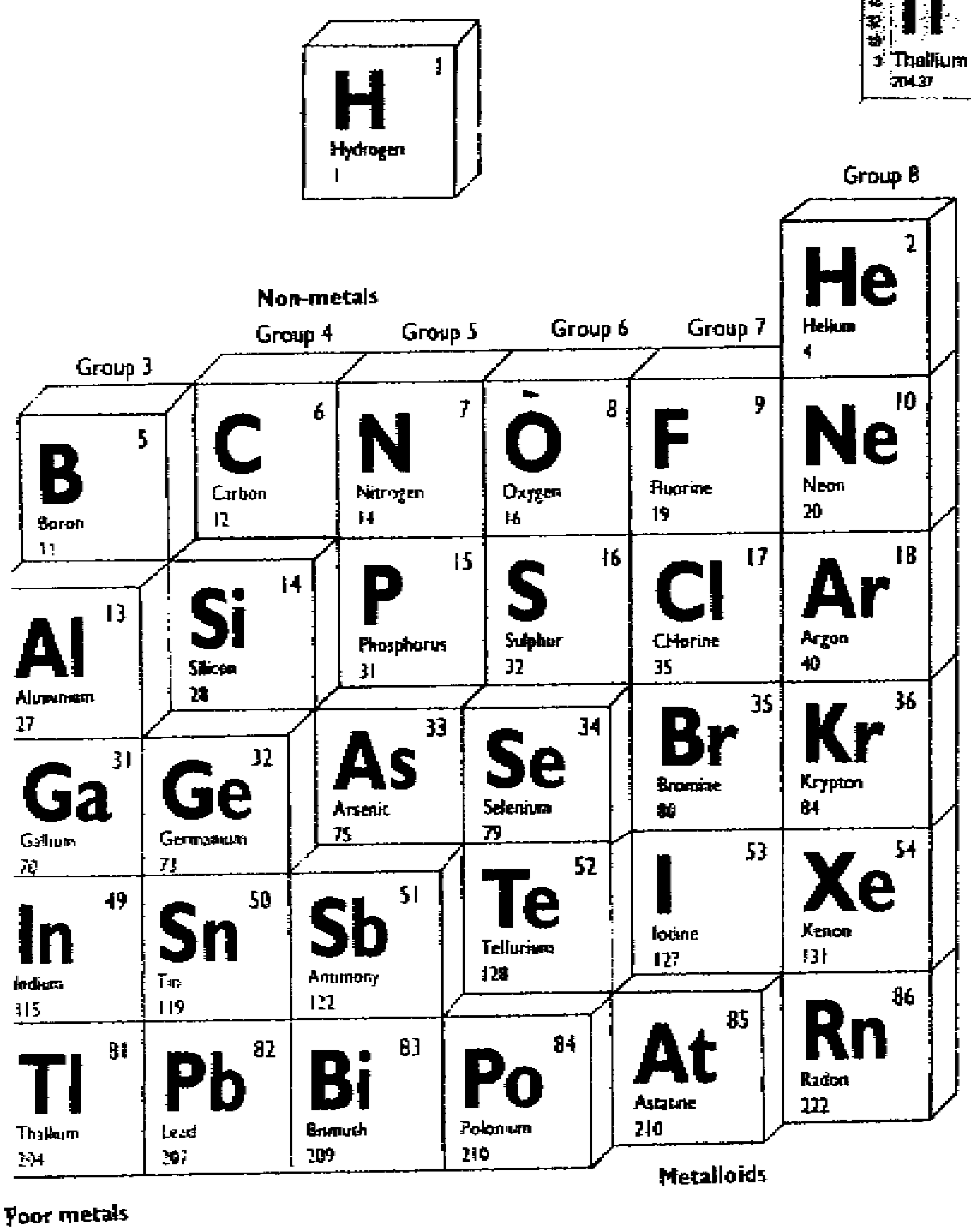


On the right hand side of the table of elements you find what are called the 1s block which consists of hydrogen and helium which are both nonmetals. The right hand column contains the inert gases (group 18).

Group 17 contains the most reactive elements such as fluorine and chlorine.

The p block are those elements which have filled only part or all of their p orbitals. The energy level is listed on the right hand side.



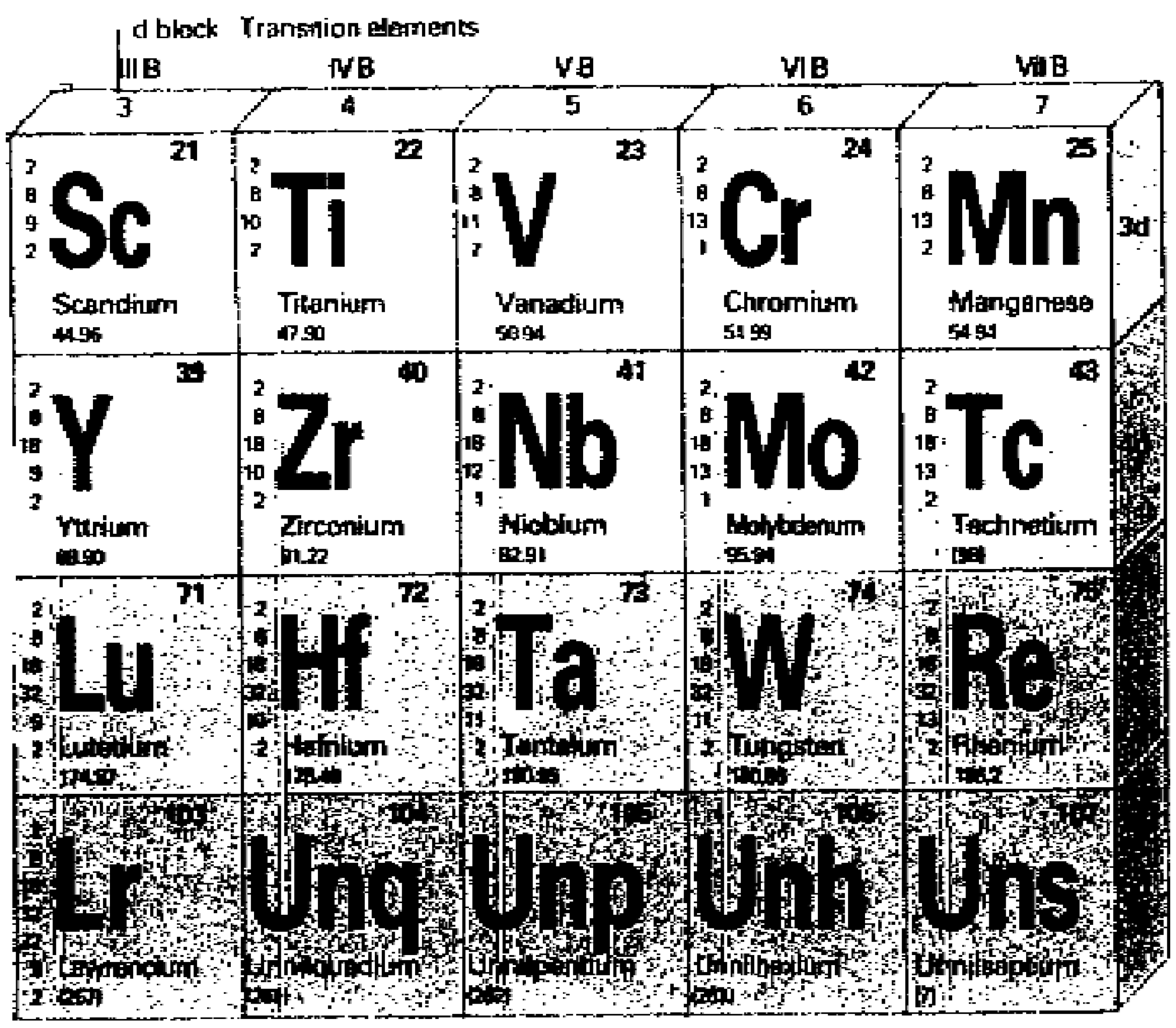


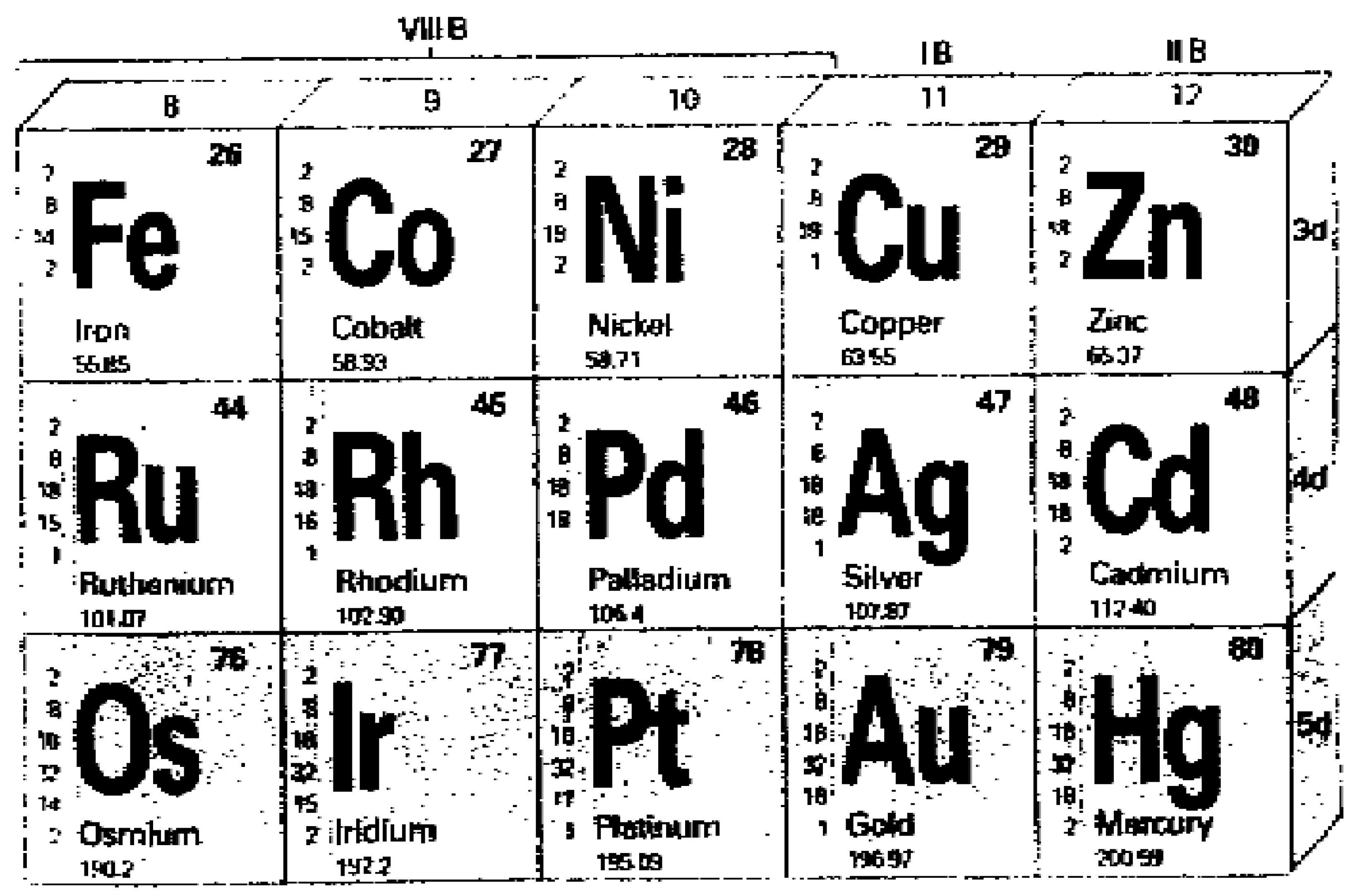
The older method of describing elements in the periodic table of elements is shown here. The upper right shows all the non metals in one shade and run diagonally from carbon to radon. The mettaloids are in the middle and often have properties of both metals and non metals.

The poor metals in the rest of the chart are similar to the true metals but lack a property needed to be called a metal.

Aluminum has both lightness and strength which makes it a valuable "poor" metal.

The following are all metals and are called "d block" elements. Many of these form poisonous salts and have been used in deliberate poisonings and found occasional use in war. The reason they have this name is that all the metals in the group will fill the d shell (underlying an outer s shell) with electrons. These elements form compounds in which they may transfer from 2 to as many as 7 electrons to other atoms.





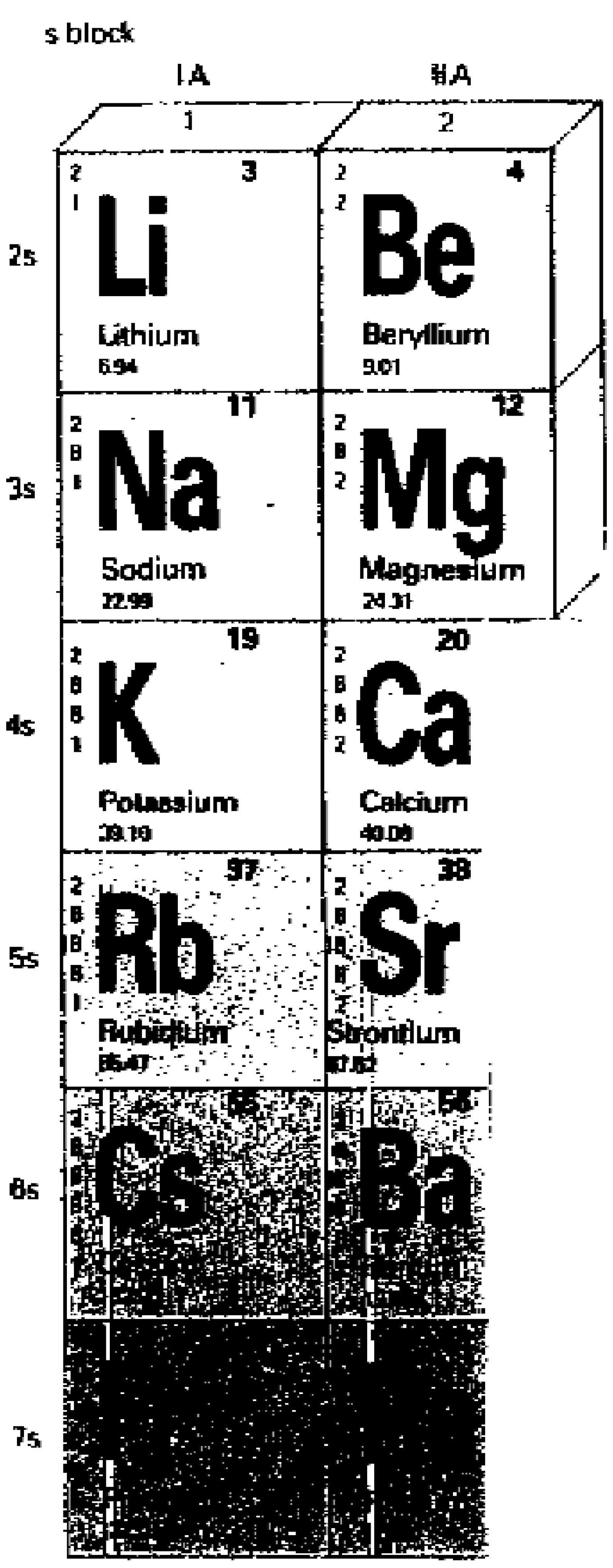
The s block is made up of

Group 1 - Alkali metals

Group 2 - Alkaline earth metals

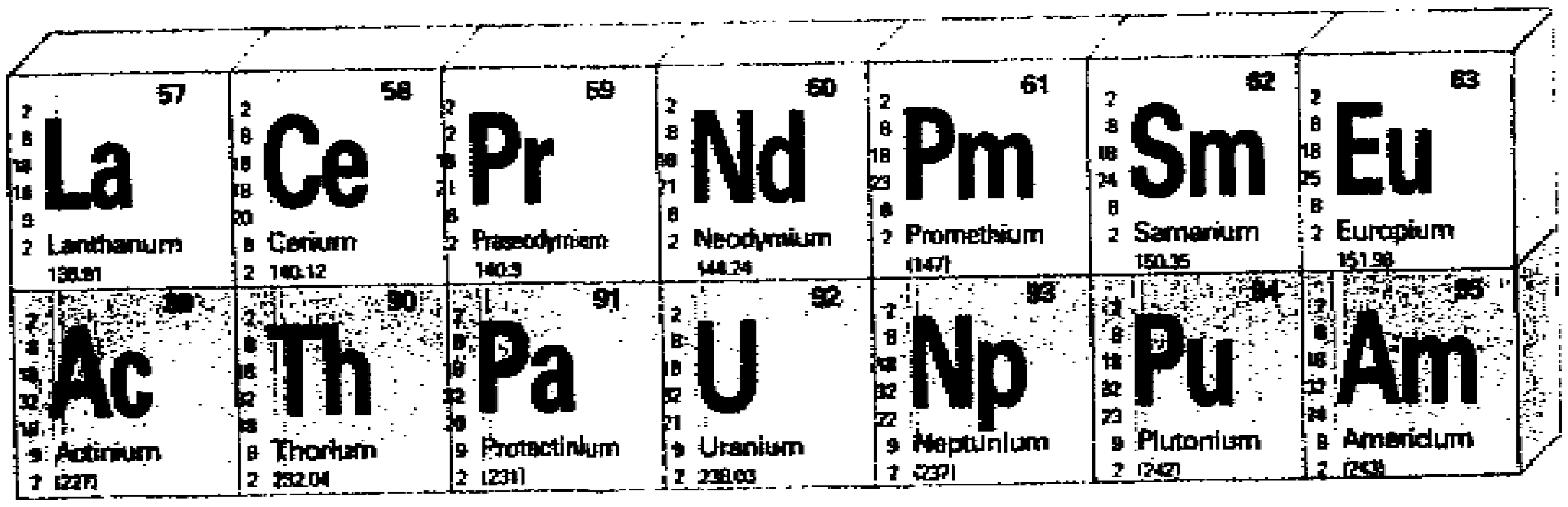
They all have one or two electrons in their outer shell that they donate to other elements which they combine with to form salts. This is how they are found in nature, as combined with other elements to form salts. A lot of energy, usually in the form of heat from a furnace is required to separate and extract the metals in pure form because the ionic bonds they form are so strong.

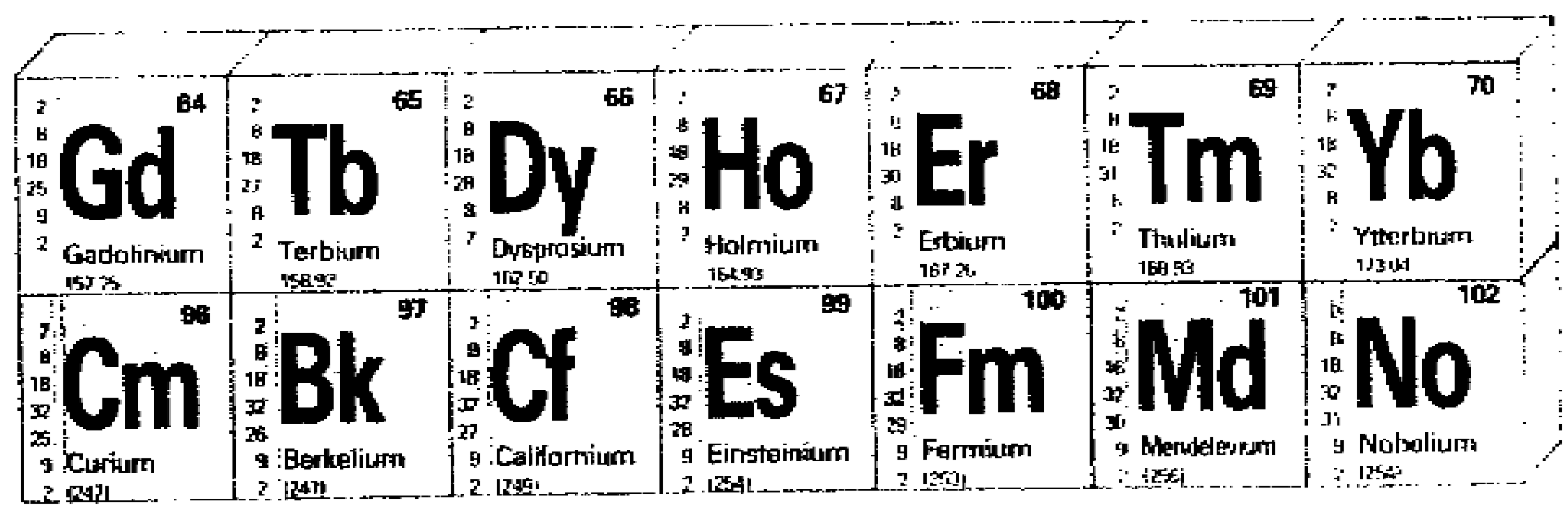
Once the metal is separated from its salt, it is often combined with oxygen to form strong alkalis like caustic soda (sodium hydroxide), or caustic potash (potassium hydroxide).



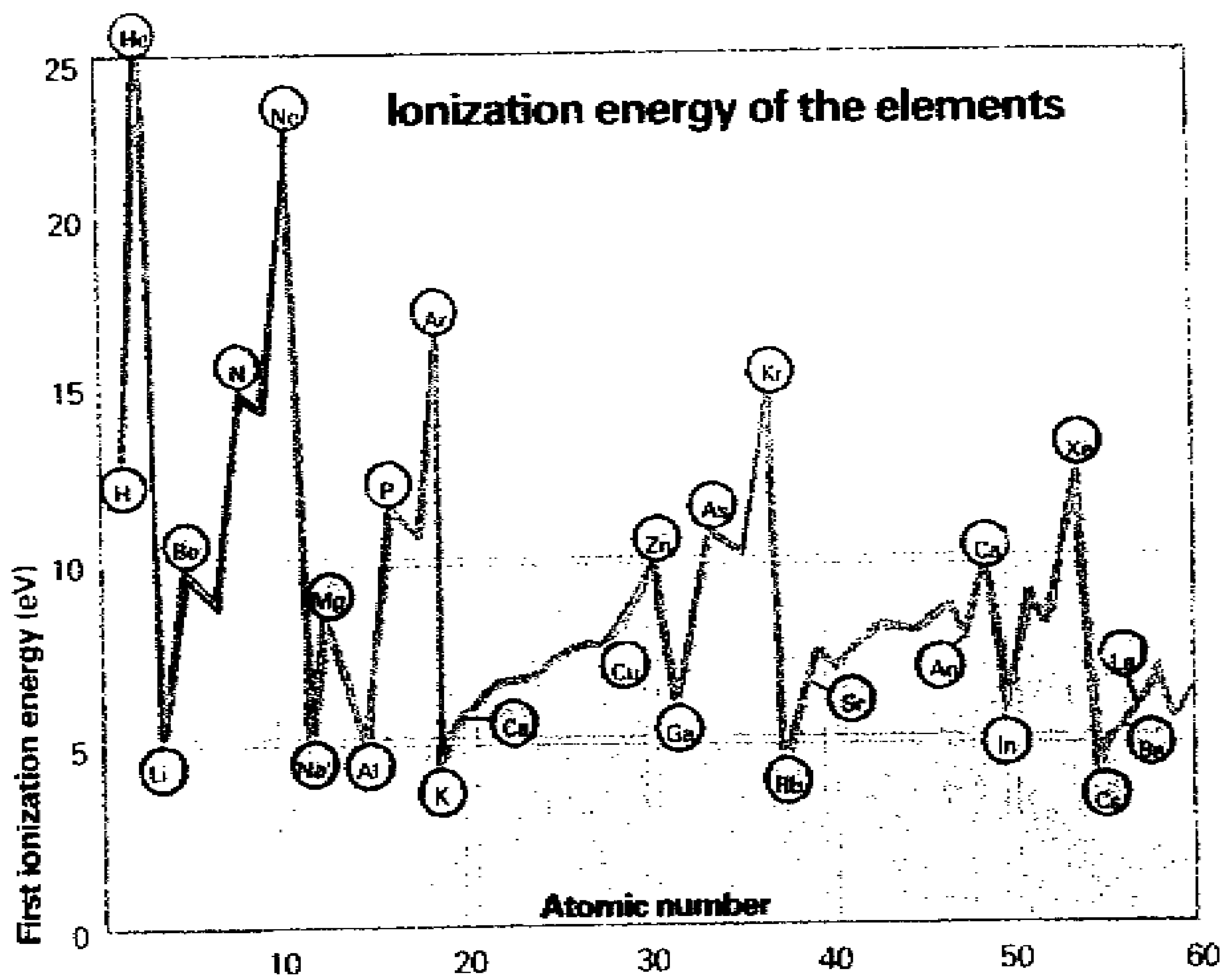
Elements 57-70 are called the lanthanides (rare earth) metals.

Elements 89-102 are called the actinides and are all radioactive. Only Uranium (#92) and Thorium (#89) are found in deposits on earth because they have long half lifes.



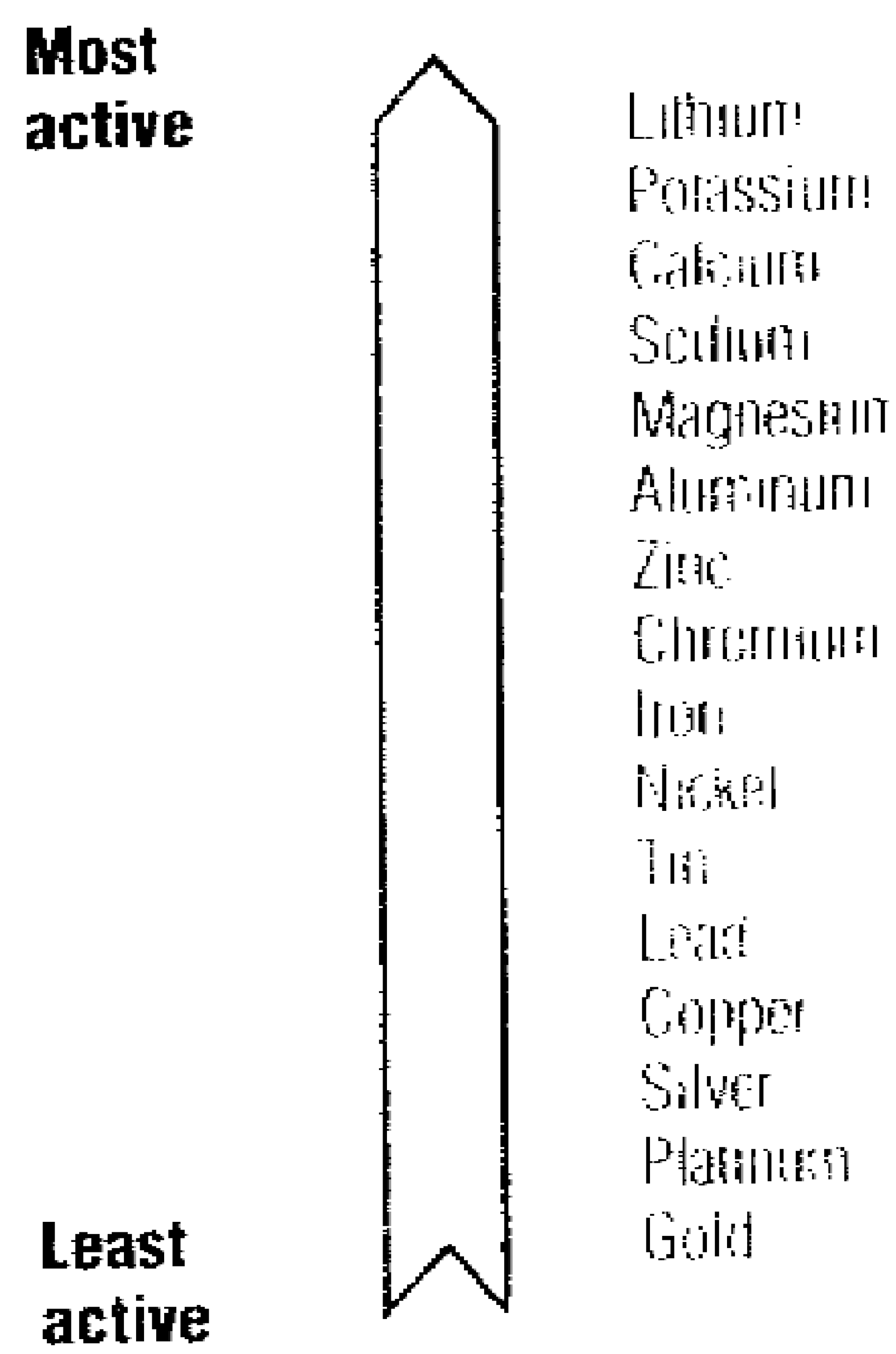


One measurable property of the elements that is consistent is the amount of energy required to pull the outermost electron away from an element. This is called the ionization energy. The elements that have a full shell do not easily give up electrons and require a great deal of energy. These are at the top of the chart as Helium, Neon, Argon, Krypton, and Xenon. As the outer shell becomes nearly empty, the energy requirement is low and generally increases as the shell fills



Another important property of elements is their activity and reactivity.

Elements like Silver, Platinum, and Gold are found pure in the earth's crust. All the other more active elements are found in compounds called ores which are mined from the ground and processed chemically to obtain the pure element.

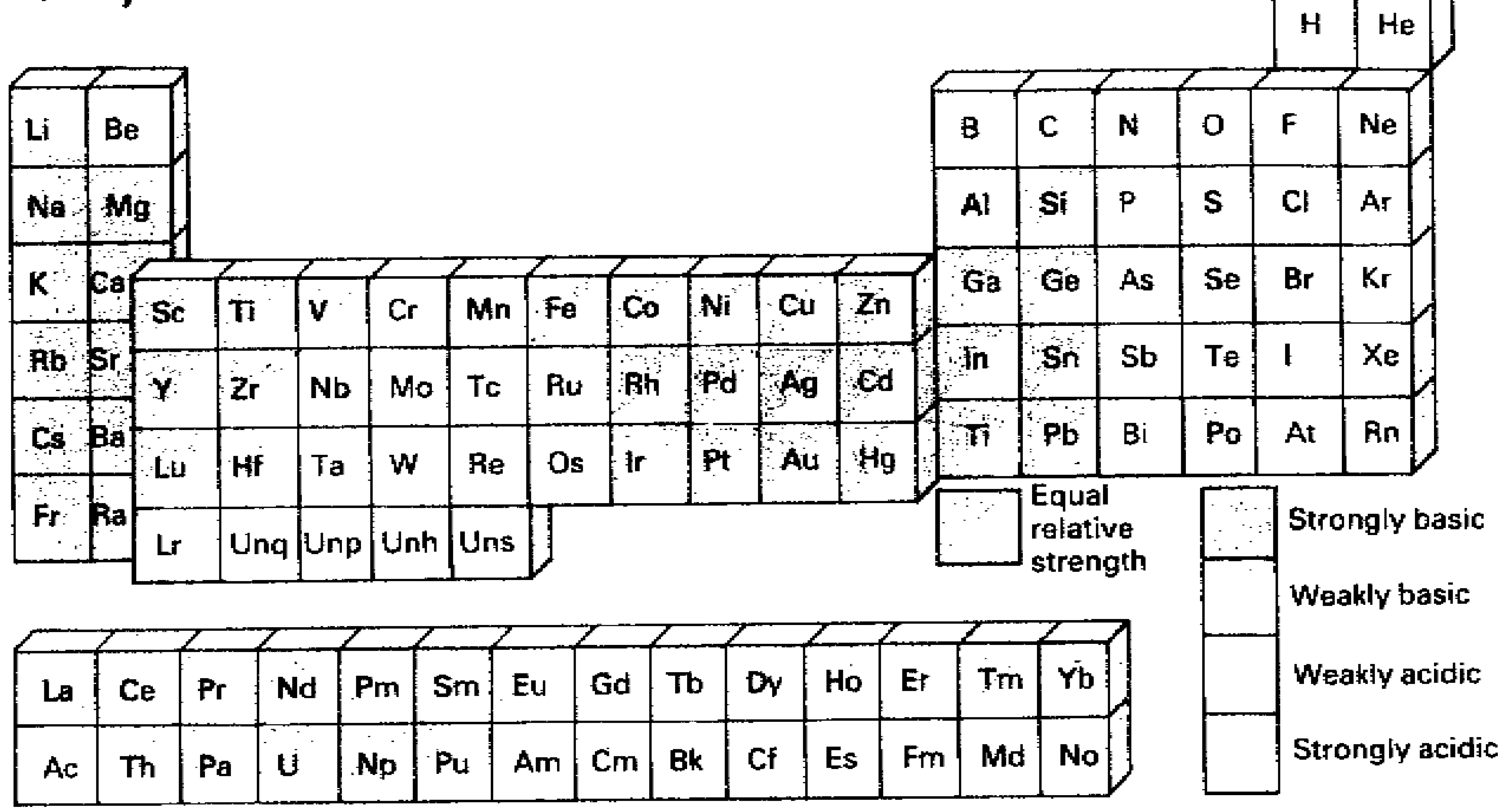


The sciences of **acids** and **alkalis** are important in chemical warfare because elements that exchange ions can attack living tissues and destroy them. An acid is a material that has many positive (+) hydrogen ions. This means that their hydrogen atoms have lost their single electron. When certain elements or compounds are dissolved in water, they produce a chemical reaction that creates large amounts of positive hydrogen ions from the hydrogen in the water and this makes the solution strongly acidic. These substances that cause these acidic reactions are called "acids". When dissolved into water, Hydrogen Chloride gas splits almost entirely apart into hydrogen and chloride ions making very corrosive hydrochloric acid. This acid, in strong solutions can react with skin tissue destroying it in seconds. Hydrogen chloride gas was widely used in WW1 to attack enemy soldiers because the gas would form the acids in the moisture on skin and in the lungs and would often kill the targets if enough gas was breathed in or covered the exposed skin. The sting of red army ants is due to the production of strong acid which is injected into the skin when they bite. Mild acids that do not injure in dilute concentrations are found in foods like oranges, lemons and other fruits. These contain citric acid. Vinegar contains acetic and or ethanoic acid that can be dangerous in strong concentrations. The strong and concentrated acids like Nitric, Sulfuric, and Hydrochloric acid are used to dissolve metals and ores in chemical processing. Sulfuric acid is used in batteries to provide hydrogen ions for electricity. Nitric acid is used to react with other materials to produce many explosives.

In an alkali solution, you have a water solution that contains negative ions most often called "Hydroxyl Ions" (OH-). These are water molecules that have lost a hydrogen ion. Instead of H2O you have HO with a negative ionic charge. Chemicals called bases can be added to water. Bases are usually a metal which splits into positive metal ions and negative hydroxyl ions when added to water. Sodium Hydroxide (Caustic Soda) is a strong base that splits into sodium and hydroxyl ions.

Almost all the elements form oxides. When these oxides are added to water, they may react with it to form basic or acidic oxides in solution. Metals produce basic oxides and non-metals give acidic oxides. Some may form both kinds of oxides such as aluminum (oxide). The following chart shows the form the elements yield in water.

Acidity

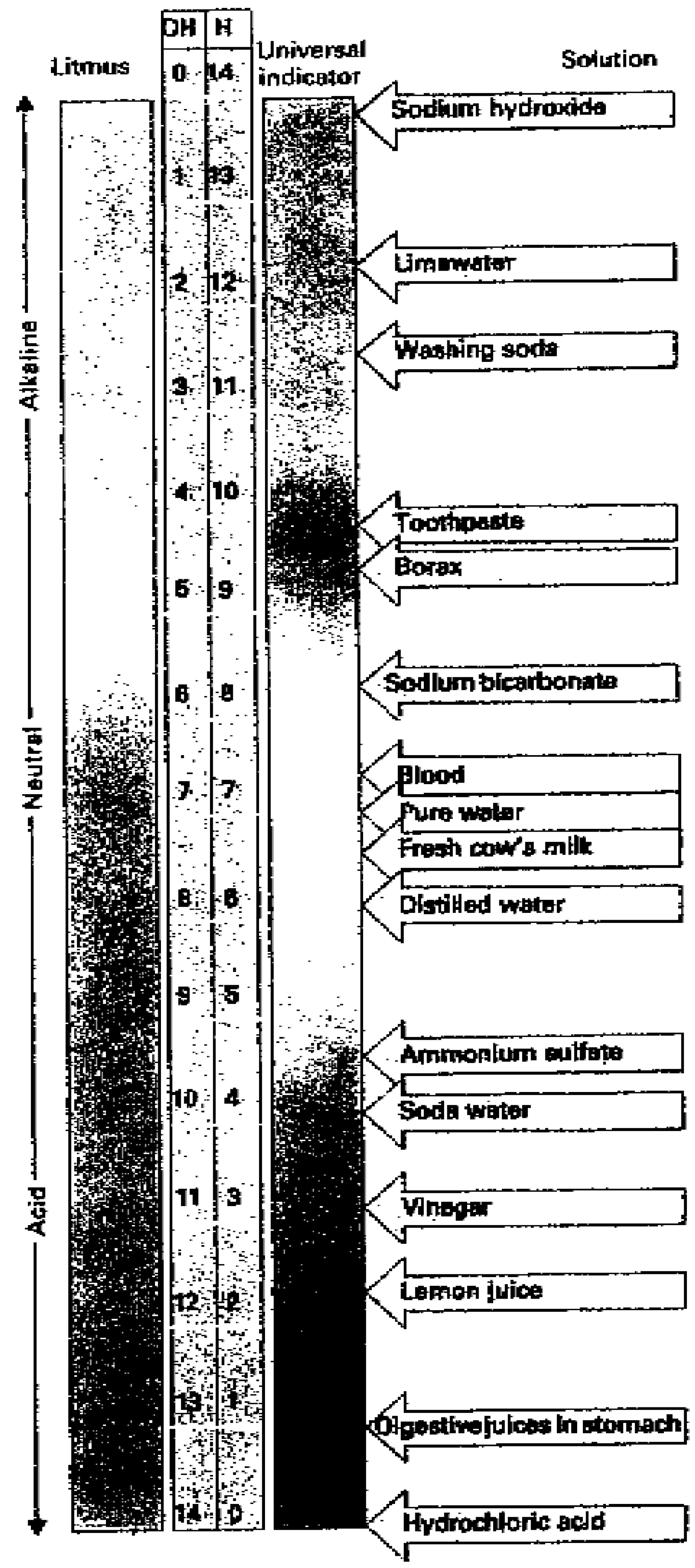


Acids can cause great damage even when they are not used in war. Acid rain is formed when carbon dioxide in the air dissolves in rain clouds to form carbonic acid. High emissions of sulfur and nitrogen oxides from industry and car exhaust make the rain 500 times more acidic then normal. This acid rain injures trees and kills off all the life in many freshwater lakes. Limestone can be added to the lakes to neutralize the acid.

Acidity and alkalinity can be measured on the **pH** scale. The midpoint of the scale is neutral or 7. Tap water is slightly alkaline with a pH of 8-9 while rain water is slightly acidic at pH of 5-6.

Each change in the pH number represents a 10 fold increase in the amount of ion strength. Vinegar at a pH of 3 is 10 times more acidic than soda water at a pH of 4. Hydrochloric acid at a pH of 0 is 100 times more acidic than lemon juice at a pH of 2.

The pH scale



When substances are brought together, they often mix and form solutions. These can be mixtures of gases, or liquids, or any form of matter mixed into a liquid which is called a solvent. Water is the most common solvent. A material that "dissolves" into it is called a solute. Our blood is a water based solution full of water soluble minerals, vitamins, proteins, and other substances. Understanding this helps in learning how poisons and other chamicals cause harm once they are absorbed into the body.

Gasoline is a solvent and many solid materials and plastics will dissolve into it. Plain tap water contains many dissolved minerals such as calcium (lime) salts which gives water its hardness, fluorine to prevent tooth decay, chlorine to kill dangerous bacteria (in tiny amounts), and so on. Water also contains dissolved air. and when it is boiled, the air comes out and the water tastes flat.

These molecules that go into solution actually are chemically separate from the water but they move into the spaces between the water molecules and are held in place (in solution) by it. When the amount of solute or salts is too great for the water to hold up in solution, all the spaces are filled and the extra solids fall out of solution forming crystal solids in the bottom of the container. By heating the water you can create more space between the molecules so the water can hold more material in solution. When the chlorate salts are made in electrochemical cells for explosives (Volumes 3 and 4), they can be separated out because the chlorates are held up in solution more easily than the remaining salt.

Solvents are used to separate chemical poisons and weapons. Ricin can be precipitated out of a salt solution of water from castor bean extract because it goes into solution (water) and the salt then crowds it out of solution. Ricin is one of the deadliest poisons known. Many of these poisons and dangerous chemicals can be separated and concentrated by using different solvents. For example, salt will dissolve in water but not in gasoline. Wax will dissolve in gasoline but not in water. A mixture of wax and salt can be completely separated by mixing them in one of the solutions where one "salts" out and precipitates to the bottom as a solid while the other dissolves into solution. The solvent can then be evaporated off leaving the purified solid wax or salt behind.

All chemicals can exist in one of three fundamental forms, **Liquids**, **Solids**, or **Gases**. All chemicals and elements under the right conditions can exist in any of these forms. Solid arsenic was used in ancient times to poison enemies. It could also be mixed into water to form liquid solutions that would poison water wells. This was used by the ancient Romans to prevent destroyed cities like Carthage from repopulating and rising up against them again. They simply added large volumes of water soluble arsenic salts to the wells that killed every person or animal that would drink from them for decades. By WW1, the German Chemists had figured out how to react alcohols, cyanide, chlorine and aromatics with arsenic to form poison gases at room temperature. Ethyl and Methyl Dichloroarsine, Diphenylchlorarsine, and Diphenylcyanarsine are a few of the examples actually used in WW1 with deadly effect.

The form that a substance can take depends on the way that the atoms are packed together. In a solid, the atoms are packed very closely together because they have low energy levels for that substance and do not vibrate fast enough to push the atoms apart. This packing is so dense that the atoms cannot move about freely and so they end up having a definite shape and volume. It also causes solids to be much denser than liquids or gases which will flow to fill the container they are in.

Most solids have a pattern that they form in called a crystal. The shape of the crystal depends on the size and shape of the particles and the strength of the bonds between them. When crystals are heated, they melt at a precise temperature into a liquid. This temperature is called the melting point. Some solids like glass and some plastics that have no crystal structure and are called amorphous.These solids have no definite melting point and gradually melt over a range of temperatures.

Solids have strong bonds between the atoms and molecules and the stronger the bonds the more they can maintain their shapes. Metals like titanium used in aircraft frames are very strong and are not broken easily. In cookies, the bonds are much weaker so the cookie crumbles easily. Repeated stress to strong metals eventually may cause fatigue and cause the metal to bend or break at a particular spot.

When a solid absorbs heat energy, its molecules vibrate faster and push or move each other farther apart. This causes the substance to physically expand and every substance has a definite rate of expansion. When the vibrations are slowed down, the substance cools and contracts because their is less vibration energy to push the atoms apart. Even all the gases in the air that we breathe can be frozen solid at 3 degrees Kelvin (-454 F or -270 C).

At a substances melting point, the particles are held together so loosely and are vibrating so fast, that it begins to flow in all directions. It has now become a liquid. This greater vibration energy pushes the atoms so far apart that liquids usually take up at least 10% more space than their solid forms. The bonds are so far apart now and so weak that they cannot hold the liquid in a definite shape so the liquid now flows and can be poured like water. They fill the bottom of the container they are poured into or flow like a river toward the lowest spot while leaving a smooth upper surface. How fast they flow depends on their viscosity or thickness. In thick viscous liquids like engine oil or glue, the bonds are strong enough to slow down the rate of flowing. The bonds in water are much weaker so the flow is much faster.

Liquid particles not only vibrate and spin on a spot, they also break away and wander around freely from each other. This is why liquids can be poured together together and mix so easily. Some of these particles are moving so fast that they acquire enough energy to escape the bonds holding them together completely. When this happens, the liquid particle evaporates into a gas. As the temperature of the liquid becomes hotter, more and more particles evaporate into the air. As this happens the remaining liquid cools slightly because the particles that escaped had more vibration energy than the rest and took it with them when they evapórated. This is why sweating on a hot day cools you down and also why damp clothing feels cold.

When a liquid turns to a gas, the particles are travelling so fast (up to 1,000 mph) and are so widely spaced that the molecular and atomic attractions cannot hold them together and they move around freely. Gases take up around 1,300 times more space than their liquid form at normal air pressures. Because gases move so fast and collide with each other billions of times a second, they exert a continuous pressure on everything around them. If you squeeze more gas particles into a smaller space, you cause more of them to hit each other in a given area, so you cause the pressure to increase.

Gases move and mix so rapidly that if you open a bottle of perfume (or nerve gas) it only takes a few seconds for it to reach the other end of the room. The particles moved and mixed into the surrounding air without even being stirred until they are evenly distributed. How fast any two gase mix together depends on how dense they are. The denser a gas, the more slowly it diffuses into the surrounding air. This rate at which gases diffuse is inversely proportional to the square root of their densities. What this means is that the less dense they are, the faster they mix. Knowing this is valuable because the faster a chemical war gas can diffuse into the air, the more quickly it can kill or injure, and the harder it is for the target to reach cover or don protective clothing in time.

At a temperature called the boiling point, all the liquid is forced into its gas state. It remains in this state until it cools below this temperature again. It is also possible to compress a gas back into a liquid under great pressure above its boiling point.

Gases will also condense as the surrounding air cools and the temperature drops. Since their is less energy to push them apart, they condense back into liquids and precipitate to the ground. In the case of water, we see it as rain. Most nerve gases have boiling points of 200 F or higher. They have to be heated to produce large volumes of gas. Most of the nerve agent remains liquid without the heat and when the nerve gas cools while it mixes into the air, it precipitates back out, usually forming oily droplets on the ground, clothes, buildings, etc.

Chapter 2

Methods of Exposure and Harm

Chemicals can be used to cause harm to people, plants, other living organisms, machines, and just about any other material if you know what chemicals to use and how to apply them. In this chapter we will examine in detail the major exposure routes for animals and people and will cover in general how chemicals can harm plants and non living materials. We will also discuss preventative measures used to protect against these exposures.

Chemical weapons, when used on a large scale, offer the means to depopulate and defoliate large areas, and even entire nations. These types of weapons are much easier and far less costly to produce than nuclear explosives while producing a comparable effect on civilian populations and leaving infrastructure intact.

Chemical weapons are generally used to -

1. To kill directly and eliminate enemy opposition. This can be done against individuals, leaders, civilians, or the military.

2. To maim or wound horribly so as to create the greatest burden and anxiety on the enemy soldiers and civilian population which has to see and care for the wounded.

3. To intensify fear in an enemy government and provoke unpopular reactions.

4. To clear an area or make it uninhabitable.

5. To poison a food producing area or the food and feedstocks, livestock, or cropland which can starve out an enemy population and act as an effective method of economic warfare.

6. Chemicals may offer the only suitable means of laying siege to enemies in fortifications, tunnels, bunkers, and jungles.

7. To incapacitate a target such as rioters, hostage takers, or lightly armed prisoners without causing permanent injury or death.

When chemical agents are used against humans they cause injuries by entering and affecting the human body in many ways. Entry areas of exposure are

Eye
Inhalation
Ingestion
Dermal (Skin Exposure)

Eye Exposure

The use of chemical weapons against the eyes is widespread and effective. Incapacitating gases and solids (like CS used at WACO) target the eyes and produce powerful irritation and discomfort. When used in war to harm, it has been found that blinding an enemy is often more efficient than killing him. The experiences of WW1 demonstrated that blinded soldiers crying for help had a terribly demoralizing effect on their buddies. The injured individuals caused great anxiety and created a huge burden for the healthy soldiers to try to treat and evacuate the injured. In this case the burden caused by the blinding effects of the chemicals was so great that it was believed to be better to blind than to kill. Some officers who observed their troops injuries and the disorder and panic it caused, actually ordered some of the injured to be shot to reduce the distractions. Shooting the wounded was an obviously greater demoralizing factor and the practice soon ended.

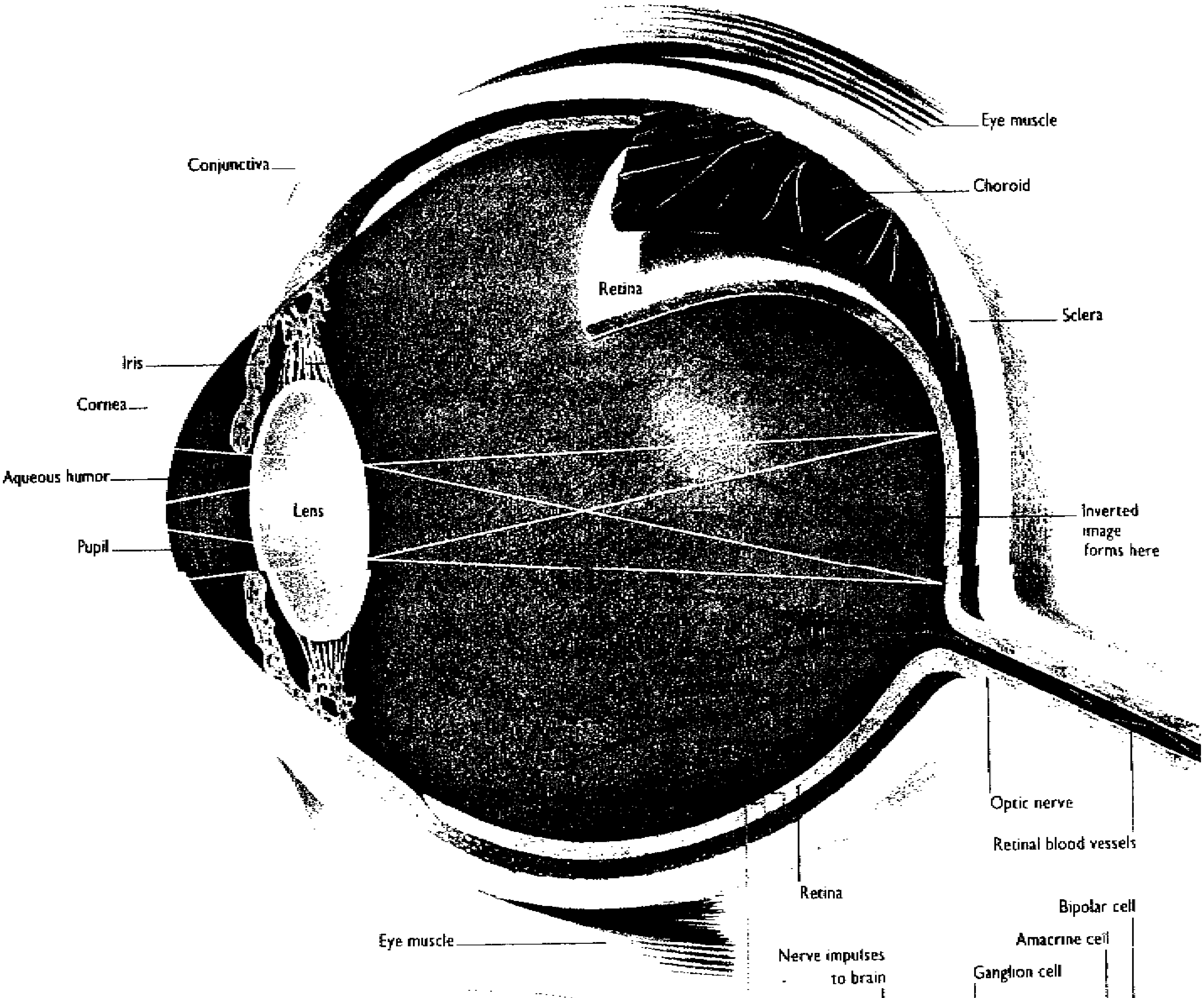
In order to understand how chemicals can cause injury or incapacitate by eye exposure, we need to show how the eye works.

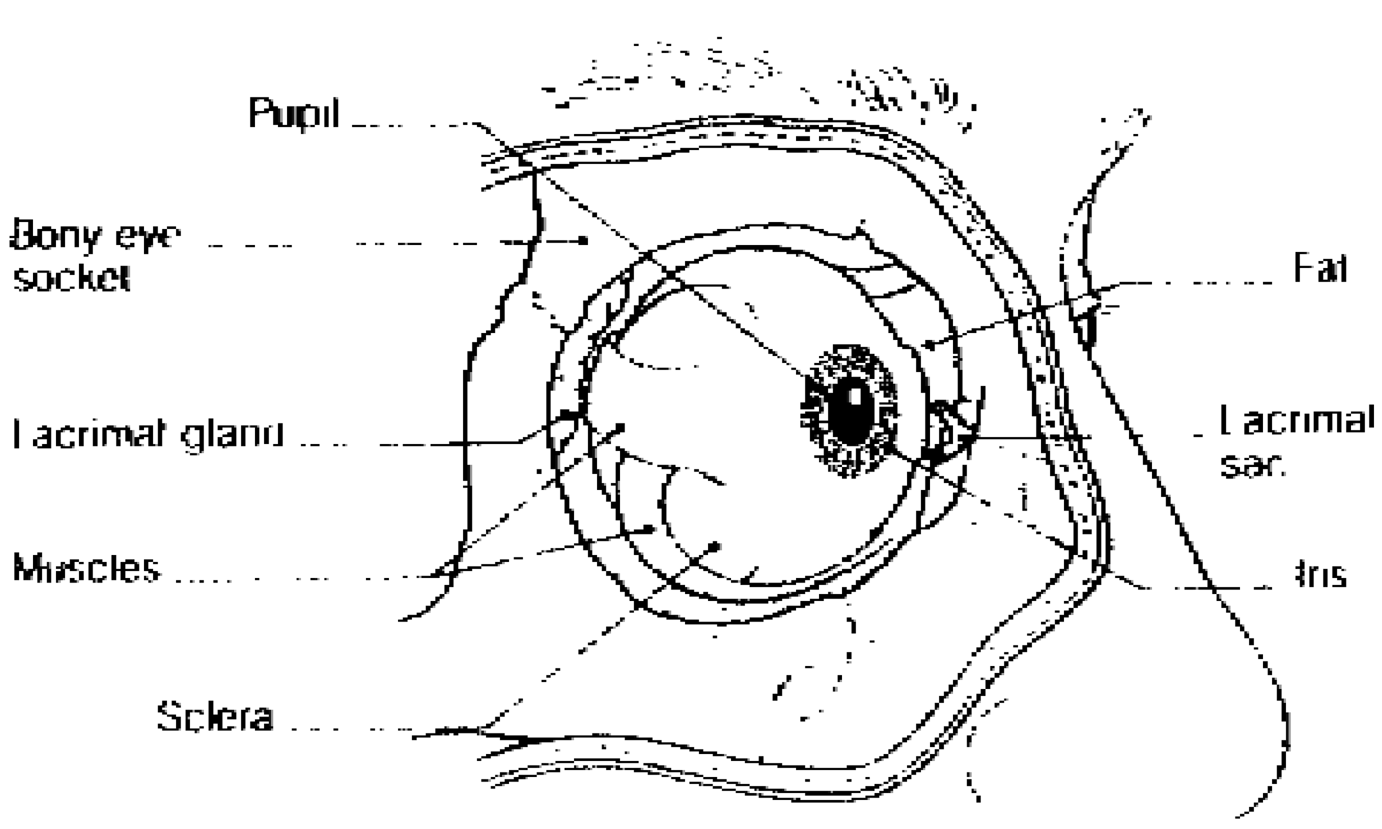
Architecture of the Eye

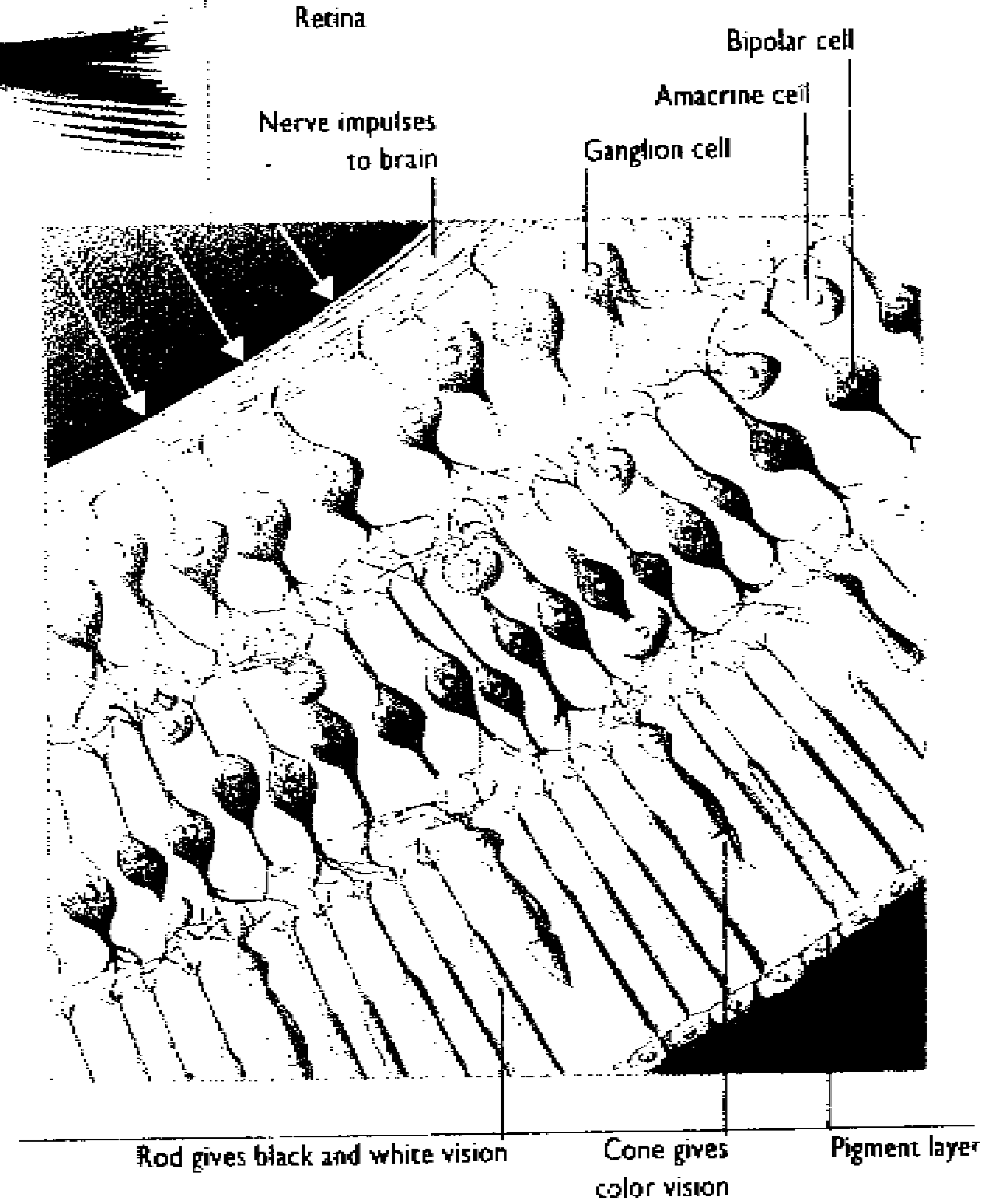
The eye is a group of structures that take in light and focus it onto the retina at the back of the eye where a network of nerves convert the image into electrical impulses that it sends to the brain. Two eyes usually work together aligning themselves on an object of attention and focus so a clear image is formed on each retina. The light rays enter through the dome like cornea at the front of the eye and pass through a lens. The eyes can sharpen and alter the focus of images by contracting the "Cilary" or eye muscles which causes the lens to become fatter to focus on near objects and thinner to focus on distant objects. In between the cornea and the lens is the pupil which narrows in bright light to protect the retina and widens in dim light so that more light can enter.

The retina contains the light sensitive cells that send out the nerve signals when the light strikes them. The 120 million rods in each eye can see only in shades of gray (monochrome). Seven million cone cells concentrated at the back of the retina see the details and color but only work in bright light. This is why we see the images in the evening and night "gray out". We see in shades of gray as the cones quit working and our eyes rely only on the rods. The retina requires a constant supply of oxygen and sugar which is why you see the branching blood vessels in eyeball photographs. The blood supplies the critical nutrients and air to keep the eyes functioning.

The eyeball lies in pads of fat inside a bony eye socket that protects it from injury. The eyeball has a tough outer coat called the Schlera (the white of the eye) that protects the cornea which is transparent. Behind the lens is a shallow chamber full of watery fluid called aqueous humor which covers the "iris" and a central hole called the "pupil". Behind the lens is the main cavity filled with a clear gel called "Vitreous Humor".


Eye muscle
Conjunctiva
Choroid
Retina
Sclera
Iris
Cornea
Aqueous humor
Lens
Pupil
Inverted image forms here
Optic nerve
Retinal blood vessels
Retina
Eye muscle


Pupil
Bony eye socket
Lacrimal gland
Muscles
Sclera
Fat
Lacrimal sac
Iris

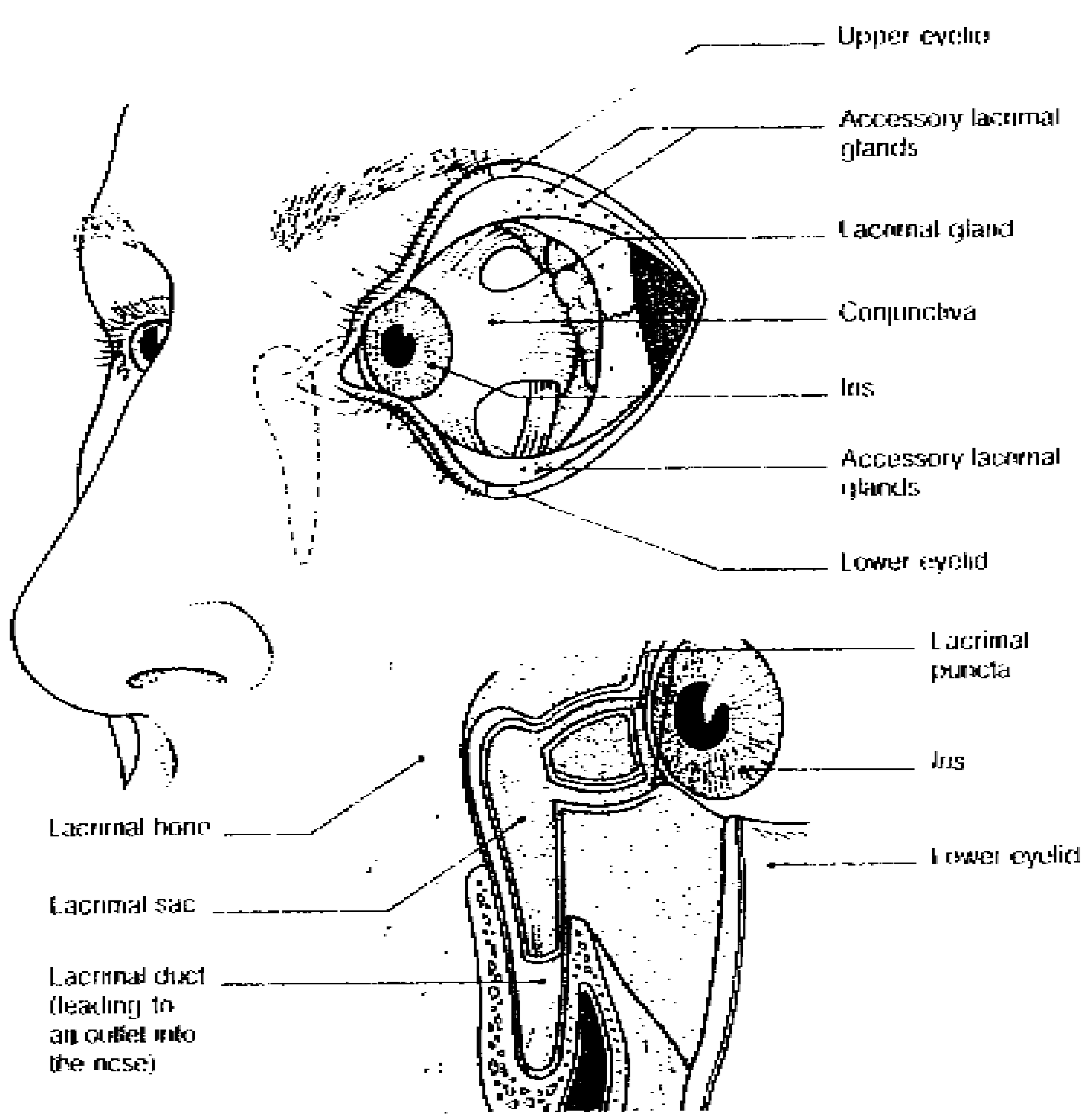

Bipolar cell
Amacrine cell
Nerve impulses to brain
Ganglion cell
Rod gives black and white vision
Cone gives color vision
Pigment layer



The eyeball is sealed off from the outside by a flexible, transparent membrane called the "Conjunctiva" which is attached to the skin at the corners of the eye and forms the inner lining of the eyelids. This permanently seals off the eyeball while allowing it to move around. The conjunctiva contains many tiny tear secreting and mucus producing glands called "Lacrimal Glands". It also contains the meibomian glands that make an oily secretion that combines with the tears to produce a three layer tear film that **must** constantly cover the cornea and conjunctiva to protect them from drying out. If they dry out, the surfaces become damaged and vision is impaired along with great discomfort.

Each eyelid contains about 30 meibomian glands that secrete an oil that prevents lid margin adhesion (the sticky stuff around your eyelids when you wake up), and forms the outer layer of the tear film. This oily layer helps prevent the moisture of the tears from evaporating. When we reflexively blink, we spread the protective oil and tears across the cornea evenly in a thin film. Without it our vision becomes unclear and if the tear film dries out, corneal abrasion and ulceration occurs which may not heal if it is severe enough. The tears also wash away foreign bodies and dust which may adhere to the conjunctiva.

The main Lacrimal glands produce tears that drain into the conjunctiva. The accessory lacrimal glands lie within the conjunctiva and secrete tears directly onto its surface. Excess tears drain through a duct that runs from the eye to an outlet in the nasal cavity. This duct is called the Lacrimal Puncta which passes into a lacrimal sac. Around the lacrimal sacs are flat muscles that compress the sacs during blinking. When we blink, we produce a suction that draws away excess fluid by compressing and releasing the lacrimal sacs. This fluid then drains into the nasal cavities.



Harm is caused to the eyes by bringing them into contact with chemicals that cause injuries or irritation. These generally come in two types -

1. Lachrymators- which are materials that are strongly irritating to the eyes. These normally produce a copious flow of tears, burning sensations, and temporary blindness but do not cause permanent damage to the eye tissues. Some of these may be toxic to other tissues in the body.

2. Corrosive chemicals that cause direct destruction by reacting with the tissues that they come in contact with. These include acids, bases, blistering agents, and many other reactive classes of chemicals.

The lachrymators were first used in organized warfare by the military forces on both sides in WW1. These chemicals generally shared the following properties-

- They would irritate only the tissues associated with the eyes and did not produce noticeable lesions. Their effects were reversible and the irritation quickly disappears.

- They are effective in extremely low concentrations (5-10 thousandths of a milligram per liter) and produce an intolerable atmosphere at tiny concentrations.

- They act very quickly producing nearly instant physiological effects. The eyes muscles contract closing the eyes forcing temporary blindness while simultaneously causing the lacrymatory glands to react and secrete a copious flow of tears.

- Most of the lachrymators are insoluble in water, but soluble in organic solvents and fats.

Most of this group are chemically related being formed around a central atom of carbon. They usually carry a halogen and one or more negative ion groups in the hydrogen atoms are readily displaced.

The WW1 lachrymators include

Ethylbromoacetate
Xylyl bromide
Benzyl bromide
Brominethylethyl ketone
Ethyliodoacetate
Benzyl Iodide
Bromobenzyl Cyanide
Chloracetophenone

Most of these are liquids which have high boiling points and low vapor pressures. This makes them mostly non-volatile materials that form persistent gases.

Modern lachrymators used by the military include CS dust (chlorobenzylidene malononitrile) used as an incapacitating agent by military and police units.

During WW1 a number of agents were used as lachrymators early in the war and it was soon discovered that they had toxic effects on other tissues of the body. These include -

Chloracetone
Bromacetone
Iodoacetone
Acrolein
Chlorpicrin
Phenylcarbylamine chloride

Some common everyday substances also cause eye injuries and make useful improvised weapons. A few examples include -

Acetic Acid- the acid in vinegar (5% Concentration) severely irritates the eyes. If concentrated and splashed into the eyes it can penetrate the cornea and cause swelling of the iris. Boiling off excess water concentrates it.

Ammonia- causes alkaline burns on most body tissues but is extremely reactive with the eye tissues. Burning of the tissues and tearing occurs and if not quickly washed out results in permanent blindness. Adding caustic soda to the household ammonia (5-10% concentrations) will cause vigorous evolution of the gas.

BCME (Bis chloromethyl ether) is produced from the mixing of hydrochloric acid and formaldehyde. It is a colorless liquid with a suffocating odor that is very irritating to the eyes in small concentrations and cause reaction damage in long exposures. It also causes cancer in exposed tissues.

Ethylene Glycol (anti freeze), when swallowed or inhaled on dust particles or from hot vapors do not directly affect the tissues but after being absorbed into the bloodstream will cause rapid eye movement, paralysis of the eye muscles, and blurred vision. These are symptoms of toxic poisoning by the anti freeze. It can be made into vapor concentrations useful as a weapon in enclosed spaces by boiling and piping into the target area.

Sodium Hydroxide has a particular reactive affinity for the eye tissues. When used as a dust, it will react with and destroy eye tissues it touches in as little as two seconds. It corrodes the fats and proteins in the eye tissue surfaces and dissolves or disintegrates them. Complete and permanent blindness almost always results. A concentration of as little as 2% in water can injure the eyes in a few seconds where the cornea is burned and and the eyelid sticks to the eyeball.

Testing for Potential Eye Weapons

In the next chapters, we will cover the production of the military developed war gases including those already mentioned. In real world situations where weapons need to be improvised in a hurry, one can often be found right on the store shelf around the corner.

When a chemical company makes any product containing a chemical that could possibly harm a person, they test that chemical for the harm that it actually causes in animals. The animals normally used in this testing for eye damage are rabbits because their eyes share many of the physical characteristics of human eyes.

The procedure for testing the rabbits are

1. A group of 6 rabbits have a measured dose of the chemical placed on the anterior surface of one eye. Usually it is administered into the everted lower lid of the right eye. The amount of the dose is .1 ml per eye which is an extremely small dose. The left eye is left as a untreated control.

2. Normally a pre anesthetic is administered 5 minutes before dosing with the chemical to desensitize the rabbits to the pain and injuries. This is usually a solution of .5% proparacaine HCl. two drops is the usual dose.

3. The eyes are left unflushed and the rabbits restrained so that they cannot remove the material by rubbing or motion.

The rabbits are observed and examined for ocular irritation and injury at 1, 24, 48, 72, and 96 hours and then at 7, 14, and 21 days by an opthalmologist. Eye irritation (reversible changes) and corrosion (irreversible tissue damage) is recorded. The results are charted with examples given below.

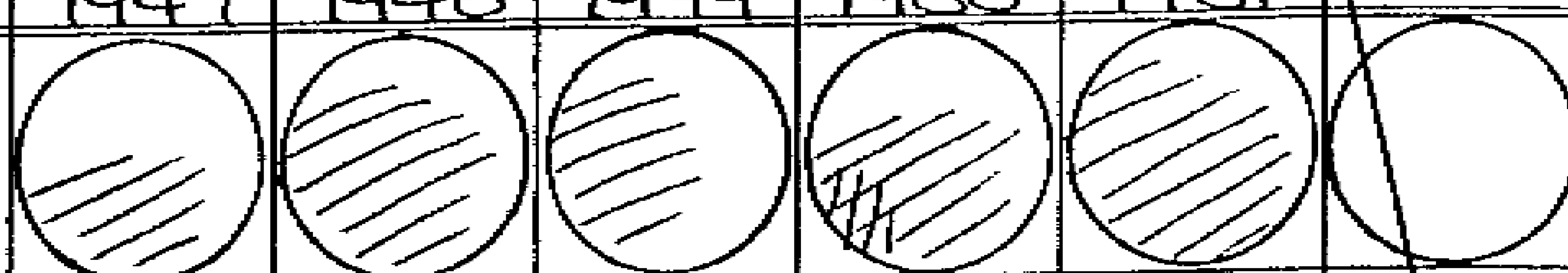
Table 1
Individual Eye Irritation Scores

Animal Number	Cornea A	Cornea B	Iris C	Conjunctivae D	Conjunctivae E	Conjunctivae F	Total Score*
			1 Hour				
F47925[t]	2	1	1[i]	2[b]	2	0	23
F47947[t]	1	2	1[i]	2[b]	2	1[c]	25
F47948[t]	1	3	1[i]	2[b]	2	2[c]	32
F47949[t]	1	2	1[i]	2[b]	2	2[c]	27
F47950[t]	2	1	1[i]	2[b]	2	2[c]	27
F47951[t]	1	3	1[i]	2[b]	2	2[c]	32
						Mean	27.7

Cornea	Iris	Conjunctivae
A - Degree of opacity B - Area of involvement	C - Degree of iridal irritation	D - Redness E - Chemosis F - Discharge

* Total score = (A x B x 5) + (C x 5) + [(D + E + F) x 2].
a Petite hemorrhaging.
b Blanching.
c Clear discharge.
d Purulent discharge.
i Injected.
j Corneal epithelial peeling.
t No pain response after test material instillation.

Observation Period: 1 HOUR

Animal Number		F4	7947	7948	7949	7950	7951	
Location of Corneal Lesions								
Cornea	Opacity		1	1	1	2	1	
	Area		2	3	2	1	3	
Iris			1[I]	1[I]	1[I]	1[I]	1[I]	
Conjunctivae	Redness		2[B]	2[B]	2[B]	2[B]	2[B]	
	Chemosis		2	2	2	2	2	
	Discharge		1[c]	2[c]	2[c]	2[c]	2[c]	
Sodium Fluorescein exam			NA	NA	NA	NA	NA	

NA Not applicable.
A Petite hemorrhaging.
B Blanching.
C Clear discharge.
D Purulent discharge.
E Hair loss around the eye.
F Possible necrotic areas.
G Unable to visualize due to severe conjunctival swelling.
H No reaction to light.
I Injected.
J Corneal epithelial peeling.
K Corneal epithelial pitting.
L Corneal edema.
M Hypopyon.
N Corneal neovascularization.
P Pannus.
R Unable to visualize due to severe corneal opacity.
S Granulation scar tissue.
POS Positive stain retention.
NEG Negative stain retention.

The point of describing all these testing procedures is that almost every chemical known has already been tested for its ability to cause harm. These tests are measured and then described on the labels used to provide safety instructions when chemicals are purchased off of store shelves or transported in bulk amounts by truck drivers. These descriptions end up on the precautionary statements and labels of the products that are sold and transported.

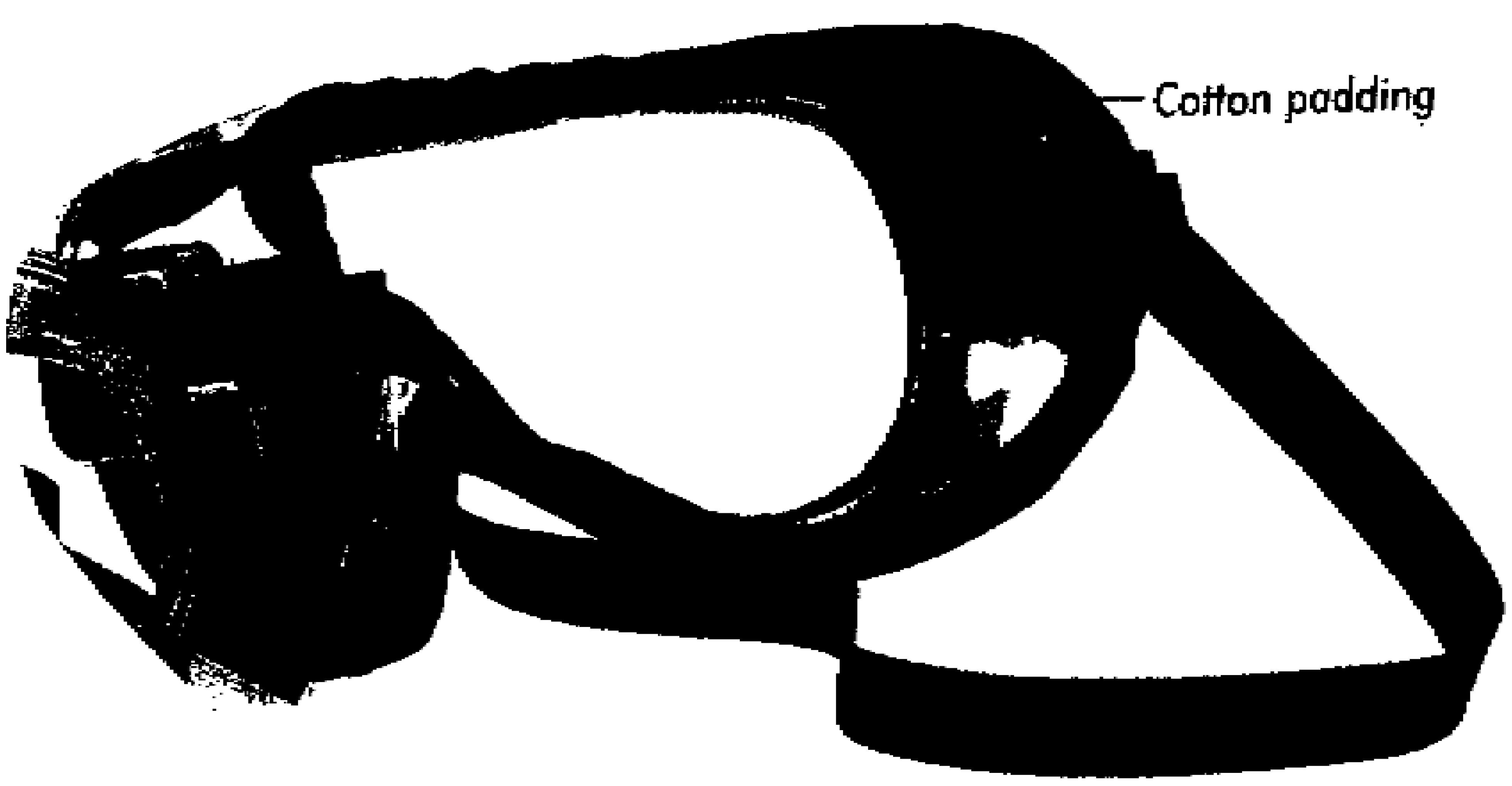
If the word on a label for a chemical is **Danger**, then it can cause permanent harm in small exposures by one of the main exposure routes. All of these routes are tested. You have to read the individual label to see if it was the dermal, inhalation, ingestion, or eye test that caused the product to be classified as dangerous. The following chart applies to the results that the chemical produces on the eyes of the test animals.

Toxicity Category	Signal Word	Precautionary Statements
1 Corrosive Irreversible destruction of ocular tissue or corneal involvement persisting for more than 21 days.	Danger	Corrosive. Causes irreversible eye damage. Do not get in eyes or on clothing. Wear goggles, face shield or safety glasses.
2 Corneal involvement or irritation clearing in 14-21 days.	Warning	Causes substantial but temporary eye injury. Do not get in eyes or on clothing. Wear goggles, face shield, or safety glasses.
3 Corneal involvement clearing in 7 days or less	Caution	Causes moderate eye injury. Wear eye protection.
4 Minimal effects clearing in less than 24 hours.	None	None required

By reading and identifying the chemical warnings on the label of available chemicals, effective weapons can be located and screened for effectiveness and use as eye irritants or injurants.

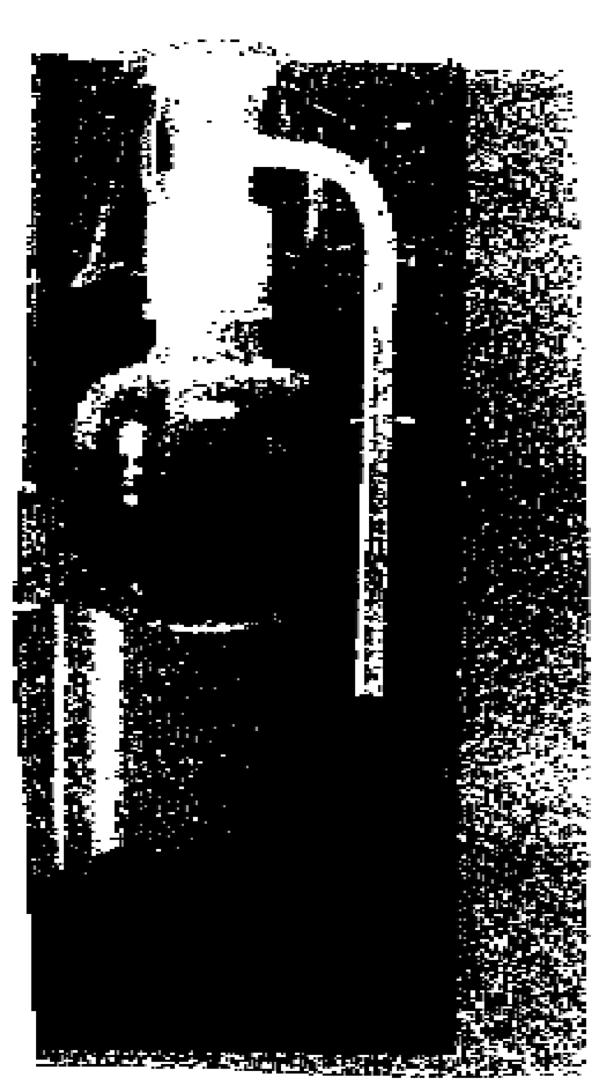
Defense against eye exposure to chemical agents

To protect the eyes and provide for full vision, protective goggles must be worn. If the potential threat is serious, a full goggle and respirator should be worn. The goggles should have a lining around the edges to keep out all dust and air. Tight fitting goggles like those worn by divers are ideal.





Secondary defenses against potential chemical attack should include a portable eye wash station and a carried bottle of water with baking soda available to help neutralize harmful destructive agents like acids. The bottle should have a tip so that it can be aimed and propel a steady continuous stream into the eyes. A shelter inside of a vehicle or room with a positive filtered air system should be available to provide refuge against chemical attack. All of these items are readily and economically available from local safety supply companies.





Inhalation Exposure

Chemicals are used in war that, when inhaled, can kill, incapacitate, irritate, anesthetize, and demoralize an enemy. Most of these are classified as lung injurants and cause damage by being inhaled into the targets respiratory system.

Inhaled chemical weapons are distributed as gases, fine mists, and finely divided powdered dusts that suspend in the air and are breathed in with the surrounding air. They act on the targets by -

1. Irritating the mucous membranes in the nose, throat, and trachea.
2. Causing direct damage to the lung tissue by reacting with the cells and destroying them.
3. By being absorbed into the respiratory system and affecting the blood gases or being distributed to the bodies tissues where they affect life processes.

The more serious war chemical agents cause massive injuries very quickly which lead to death in a few minutes or hours. The earliest war gases to injure by inhalation were developed and used in WW1. The first were simple lung injurants derived from chlorine that damaged the tissues directly by forming acids or other highly reactive compounds when inhaled. These included -

Chlorine	Methylsulfuryl Chloride
Ethylsulfuryl Chloride	Monochlormethylchloroformate
Dimethyl Sulfate	Perchlormethylmercaptan
Phosgene	Trichlormethylchloroformate
Chlorpicrin	Phenylcarbylamine Chloride
Dichlordimethyl Ether	Dibromodimethyl Ether

A second group of chemicals called the toxic lung injurants were developed based around arsenic and produce a systemic poisoning effect due to the arsenic they contain. These include -

Phenyldichlorarsine	Ethyldichlorarsine
Phenyldibromarsine	

Another class of extremely toxic chemicals based on organophosphates were developed prior to and during WW2 and would kill in very tiny concentrations when inhaled. These are called nerve agents and will be covered in depth later in this book.

The Science of Breathing Air

When we breathe in air, some of the air is diverted into the upper nasal cavity and olfactory cleft. As the air eddies and swirls, airborne molecules (and chemicals) settle onto the olfactory epithelium and are often dissolved into the mucous. The olfactory epithelium contains millions of tiny sensory nerves with bunches of tiny hairs on them called cilia. These are surrounded by fat supporting cells covered with small fingerlike projections called microvilli. When we smell odors, the cilla are stimulated and send nerve signals to the olfactory bulb in the nasal cavity roof which then interprets them and sends them along to the brain. This is how we smell. By smelling bad food or poisonous gases we can protect ourselves by sensing something alarming and taking protective measures.

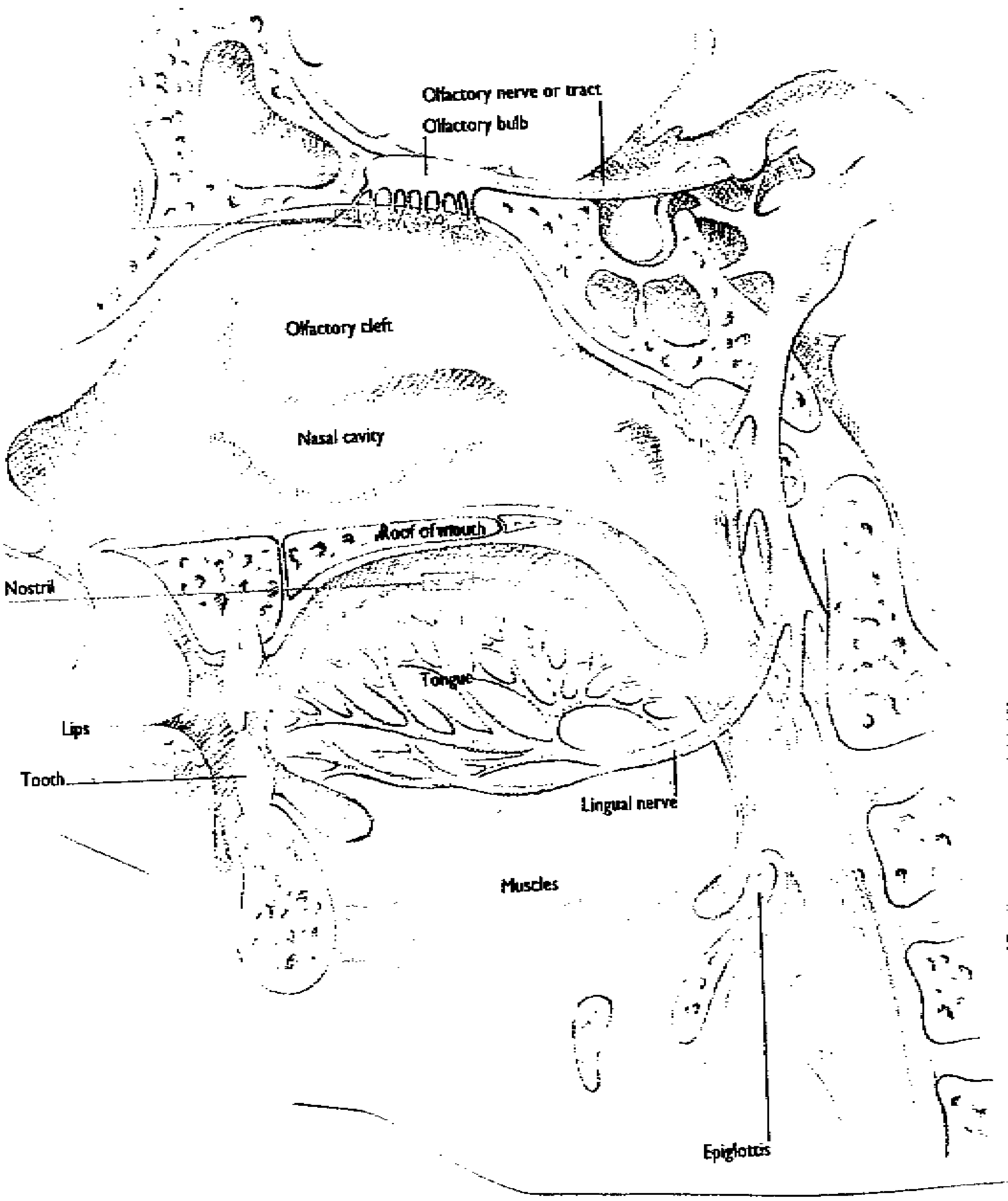
At the same time the chemical alarms are going off in the nasal cavities, the inhaled materials are passing through the mouth and into the throat and trachea. Mucous membranes and nerve cells are very sensitive to harmful chemicals and pass along these sensations as pain.

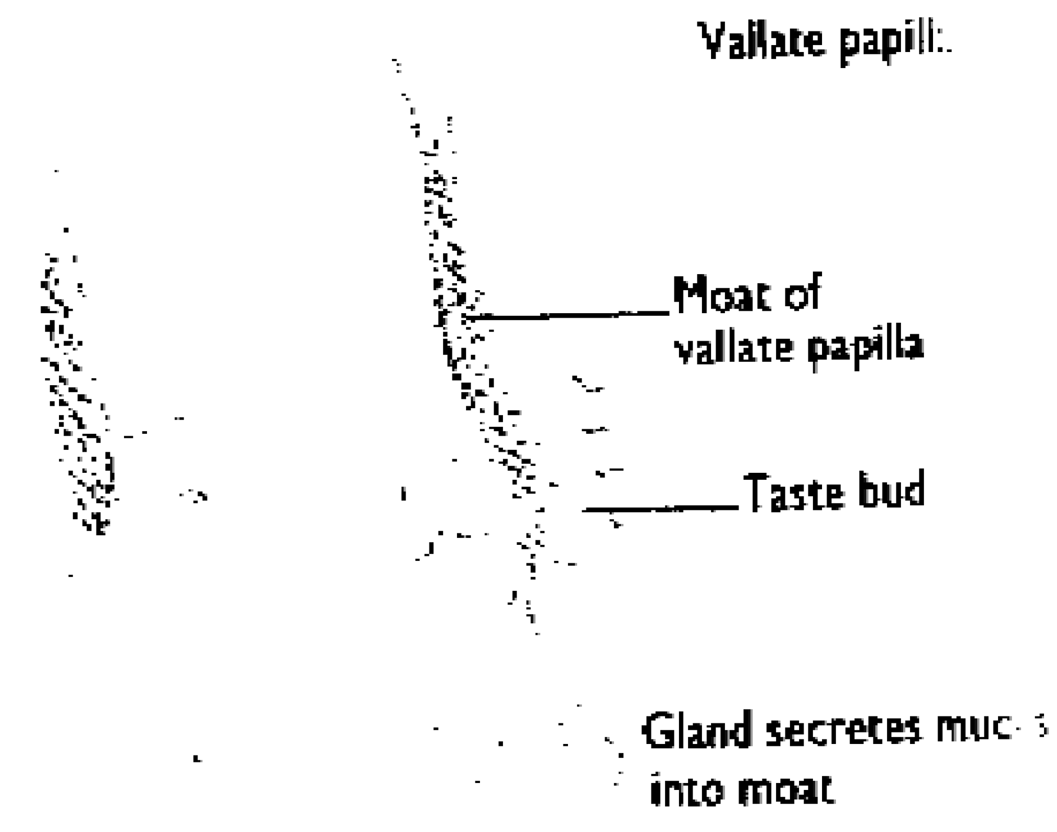
Once the air has reached the lungs, it enters the alveoli (tiny air sacs) where the oxygen diffuses from the air passing through a membrane and into the blood vessels surrounding the alveoli. Any chemicals in the air will also enter the alveoli. If they can chemically react with the tissues they can destroy the membranes and cause the alveoli to fill with blood. If this bleeding is serious enough the victim can suffocate from the injuries. The chemical injuries also cause great pain.

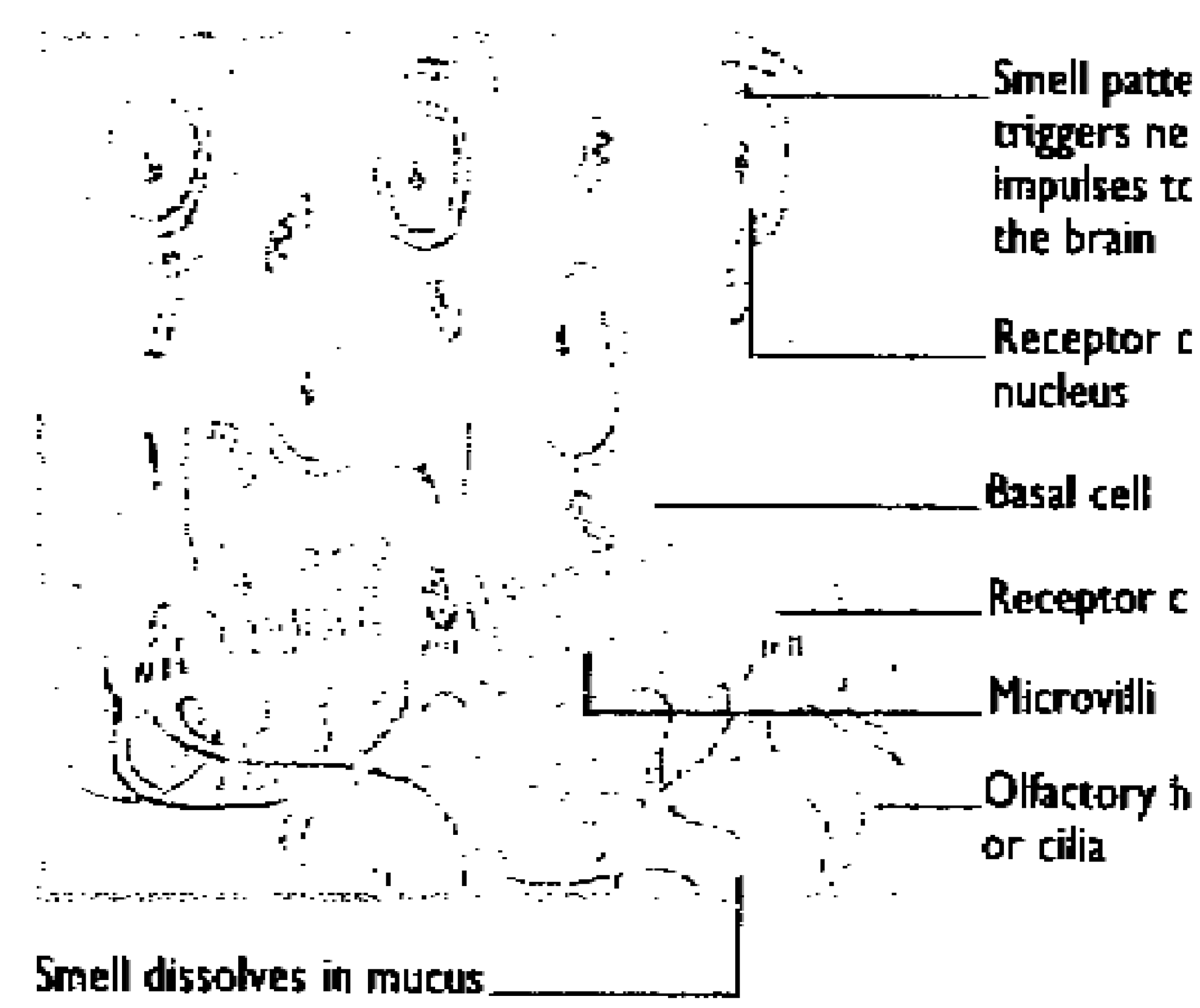
Once the oxygen has been exchanged and passes into the blood stream, the blood is pumped through the pulmonary veins into the left side of the heart. If the chemical does not react with the tissues but carries a poison like arsenic, it will travel with the oxygen in the bloodstream where the circulatory system will distribute it throughout the body.

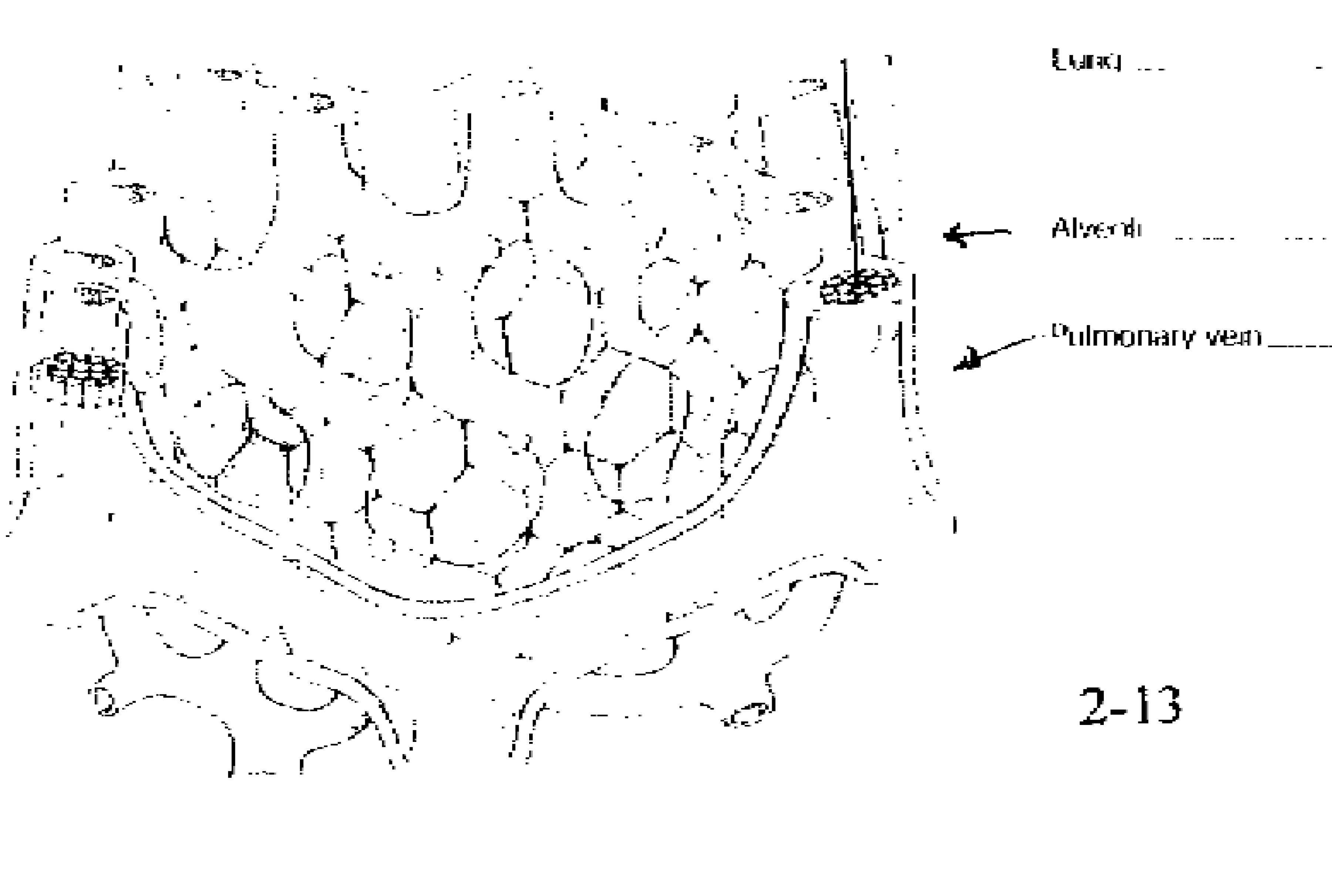
The red blood cells normally carry the oxygen to the body tissues. Some poisons like carbon monoxide will displace the oxygen in the cells and slowly cause the body to starve for oxygen. Other poisons will be carried in the fluids and find various sites and tissues to be absorbed into. In normal breathing the blood passes through tissue capillaries and give up oxygen and other nutrients from the stomach. The cells then pick up cellular waste like carbon dioxide and water and carry it back to the lungs where the water and carbon monoxide pass through the alveoli and are breathed out as waste.

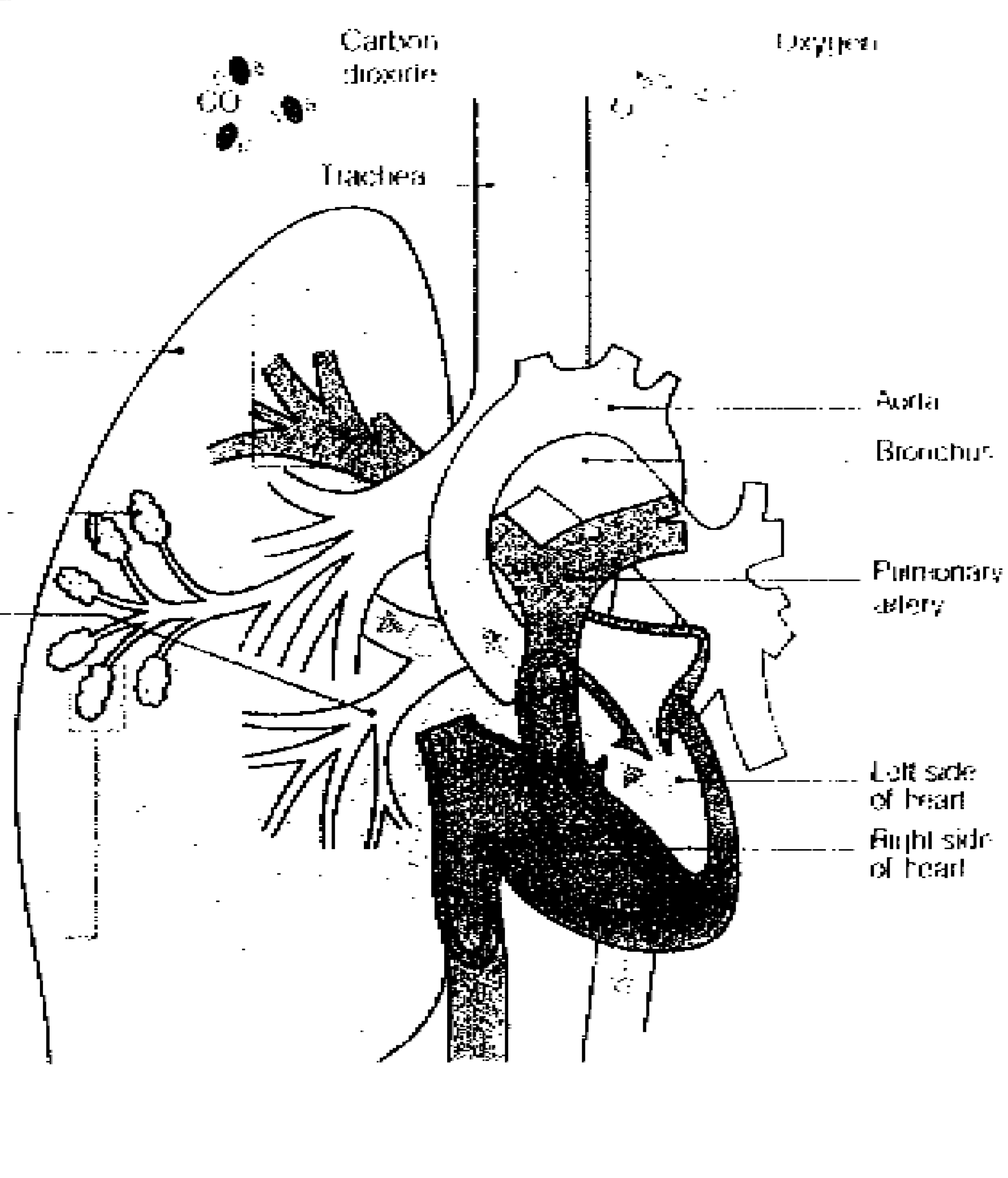
The body increases its respiration rate as it begins to work to supply the muscles with adequate oxygen. If poisons are in the air, the rate of chemical exposure also increases which can cause more harm. If the targets are forced to don and wear gas masks for an extended period to protect themselves, they have to use a great deal more energy just to breathe. The mere presence of chemicals can have a huge inhibiting effect on enemy activity because of the extra work required just to wear and move in protective equipment.


Olfactory nerve or tract
Olfactory bulb
Olfactory cleft
Nasal cavity
Roof of mouth
Nostril
Tongue
Lips
Tooth
Lingual nerve
Muscles
Epiglottis


Vallate papill
Moat of vallate papilla
Taste bud
Gland secretes muc into moat


Smell patte triggers ne impulses tc the brain
Receptor c nucleus
Basal cell
Receptor c
Microvilli
Olfactory h or cilia
Smell dissolves in mucus


Alveoli
Pulmonary vein


Carbon dioxide
Oxygen
Trachea
Lung
Aorta
Bronchus
Pulmonary artery
Left side of heart
Right side of heart

Some common materials cause lung and inhalation damage when breathed in. These include -

Ozone and particulates found in ordinary air pollution. These have been found to cause asthma, respiratory infections, and reversible damage to lung tissues.

Sulfur dioxide from air pollution which forms sulfuric acid in the lungs and cause small injuries.

Nitrogen oxides cause minor and major injuries that can lead to rapid and lethal lung infections. Nitrogen dioxide is a deep lung irritant that damages the delicate cells lining the lungs. It causes no symptoms until the damage is done when 5-72 hours later a progressive inflammation sets in leading to pulmonary edema.

Dioxins, asbestos, and cadmium can cause cancers when inhaled over long periods.

Lead dust can cause deadly nervous system disorders.

Benzene fumes can cause leukemia.

Carbon monoxide can cause light headedness, heart disease and death and when used as a weapon can be very effective (see Dr. Kevorkian).

Ammonia injures and burns mucous membranes in the nose and throat, causes pain in the lungs, nausea, and coughing. If not quickly killed, the lungs fill with fluids (pulmonary edema)and if the individual survives, pneumonia will likely set in. The ammonia reacts with moisture in the tissues to cause alkaline burns.

Asbestos, if breathed in as tiny fibers suspended in the air can cause a variety of cancers with nearly 100% mortality rates.

Beryllium dust, when breathed in causes inflammatory lesions in the lungs. It can be burned to produce Beryllium oxide gas (fumes) which work just as well. The particles are deposited in the lungs and nodules form around them. This also produces immune responses, fibrosis, emphysema, cancer in some cases, and death.

BCME described in causing eye injuries also lung tissue and can cause cancer in these tissues. Short term exposure can result in coughing up blood and breathing difficulties.

Nickel is a metal that when breathed in as a dust (or liquid mist as nickel carbonyl) causes allergic reactions, asthma, and severe nasal injuries such as perforated septa and chronic sinus infections. It is also implicated in cancers of the lung, nasal passages, and voice box (larynx).

Testing for Inhalation Weapons

When chemicals are evaluated by US EPA for potential inhalation hazards, very specific procedures are followed. Since we are concerned only with those chemicals that can be used as inhalation weapons, and they must work quickly to be effective as weapons we will describe only the acute testing procedures.

The minimum concentration in air to be tested must be at least 5 mg. per liter of air. If you are using a solid poison, it must be ground fine enough to produce a suspension in air that can be maintained with fans or aerosol equipment over a four hour period. In the case of liquids, fine atomizers are used at the end of a pump, hose and spray system. These atomizers are much finer than the finest shower head and produce tiny mist droplets that can stay suspended in air for long periods of time. If a gas is used it is simply pumped into the room or cage at the dose desired.

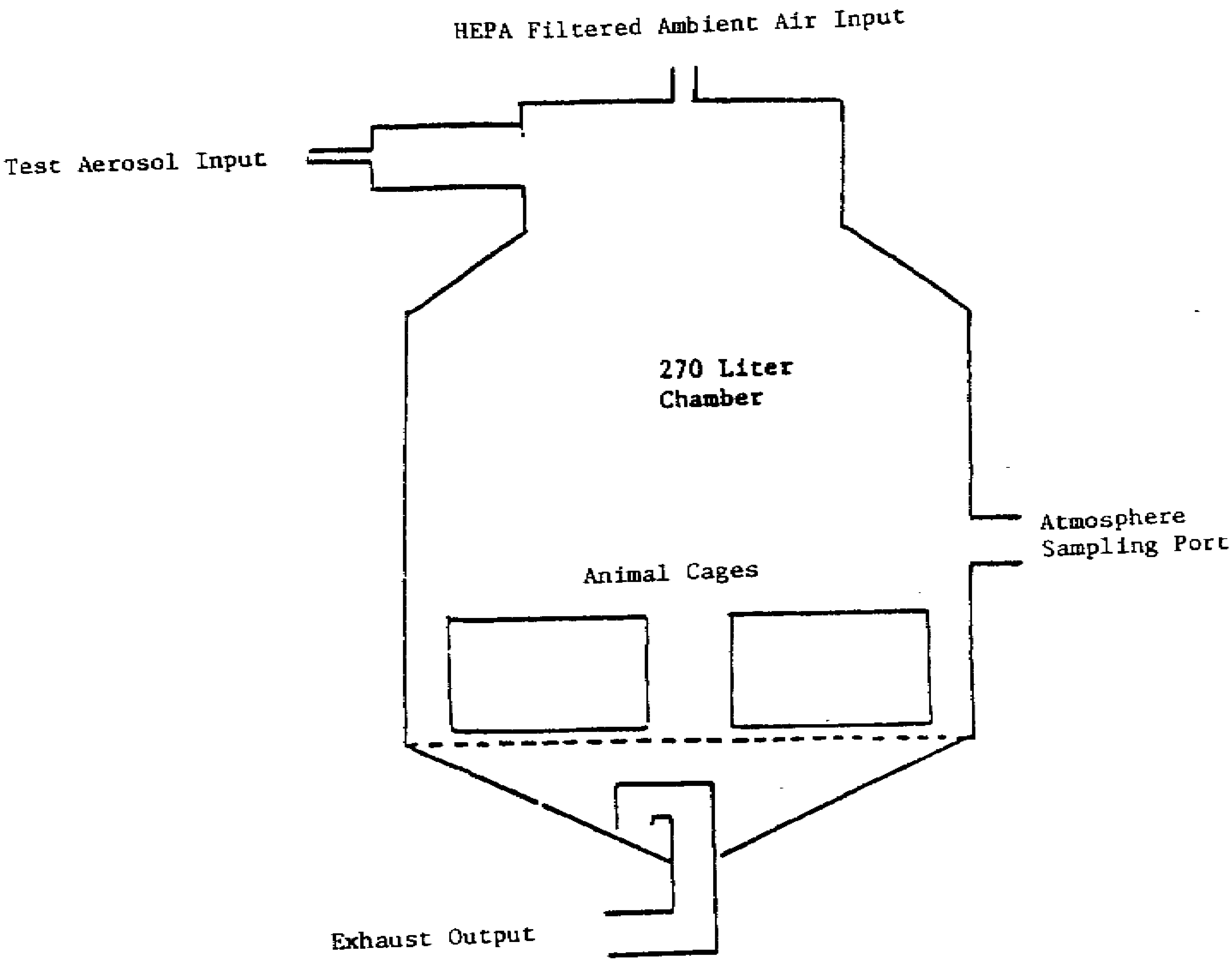
One group of five male and five female rats are dosed for four hours at the minimum of 5 mg. per liter of air (which is a very small amount) to see what the effects are. They are placed in a chamber and the air is circulated through a pump in such a way that the minimum dose is maintained. Following this exposure, the rats are observed daily and weighed weekly to see what effects the chemical has had upon their mortality, activity, body weight, and appetite. At day 15, all the animals are given a gross necropsy (autopsy). This includes careful examination of the facial area, mouth, nasal cavities, lungs, and throat. Other internal organs are examined if evidence of a systemic poison is observed. The waste products of the animals are also observed for any unusual characteristics.

[It may sound silly, but there are definite differences in harm by chemical exposure between the sexes with some substances and that is why both male and female rats are tested. In the self foaming root killer I developed we found it killed male rats when ingested at about half the dose that it killed female rats. I always thought this was just another form of perverse justice in which, not only does the female get 1/2 of everything a man works for including all the kids after a divorce, nature also gives them a built in superior ability to survive a full scale chemical strike (presuming the other side is using my root killer and the population is all turned into rats).]

When you are developing weapons to be used as inhalation chemicals, you increase the aerosol dose in the exposure chamber until you are able to kill 50% in the test animals in the desired time period. This gives you the LC 50 in air of the chemical for the time of exposure you finally reach. For many chemicals, you can have short exposures and still reach 50% mortality rates within a few hours as the damage that sets into the lungs is irreversible and untreatable. All it takes is patience. Some chemicals can kill very quickly such as nerve agents.

Once the testing is complete, the animals can be killed with car exhaust (carbon monoxide) so that their tissues remain unchanged and you can examine what sites are affected with inflammations, necrosis, etc. They are also killed by decapitation as illustrated in our lab supplement to this encyclopedia set.

A typucal chamber used in this type of testing is illustrated below.



Inhalation Chamber Design

Physical observations of the animal are reported by observations and graded as to severity. The following are examples from one such study.

ACUTE INHALATION TOXICITY STUDY IN RATS
INDIVIDUAL CLINICAL OBSERVATIONS
STUDY DAYS: 1 THROUGH 15

ANIMAL	SEX	GROUP	CATEGORY	STUDY DAY	GRADE	OBSERVATIONS
661	F	3.33 MG/L	NOSE/MOUTH	1	P	DARK MATERIAL AROUND MOUTH
			NOSE/MOUTH	1	P	DARK MATERIAL AROUND NOSE
			BODY	2	P	URINE STAIN
			EYES	2	P	DARK MATERIAL AROUND EYE(S)
			NOSE/MOUTH	2	P	DARK MATERIAL AROUND NOSE
			BODY	3	P	TAIL STAIN GREEN
			BODY	4	P	TAIL STAIN GREEN
			BODY	5	P	TAIL STAIN GREEN
			BODY	6	P	TAIL STAIN GREEN
			BODY	7	P	TAIL STAIN GREEN
			BODY	8	P	TAIL STAIN GREEN
			BODY	9	P	TAIL STAIN GREEN
			BODY	10	P	TAIL STAIN GREEN
			HAIRLOSS	13	P	RIGHT HIP
			HAIRLOSS	13	P	LEFT LATERAL ABDOMINAL
			HAIRLOSS	13	P	LEFT LATERAL THORACIC
			HAIRLOSS	14	P	RIGHT HIP
			HAIRLOSS	14	P	LEFT LATERAL ABDOMINAL
			HAIRLOSS	14	P	LEFT LATERAL THORACIC
			HAIRLOSS	15	P	RIGHT HIP
			HAIRLOSS	15	P	LEFT LATERAL ABDOMINAL
			HAIRLOSS	15	P	LEFT LATERAL THORACIC
662	F	3.33 MG/L	ACTIVITY	1	P	SALIVATION
			BODY	1	P	URINE STAIN
			BODY	1	P	URINE STAIN
			EYES	1	P	DARK MATERIAL AROUND EYE(S)
			EYES	1	P	SWOLLEN EYE LID(S)
			EYES	1	P	DARK MATERIAL AROUND EYE(S)
			EYES	1	P	SWOLLEN EYE LID(S)

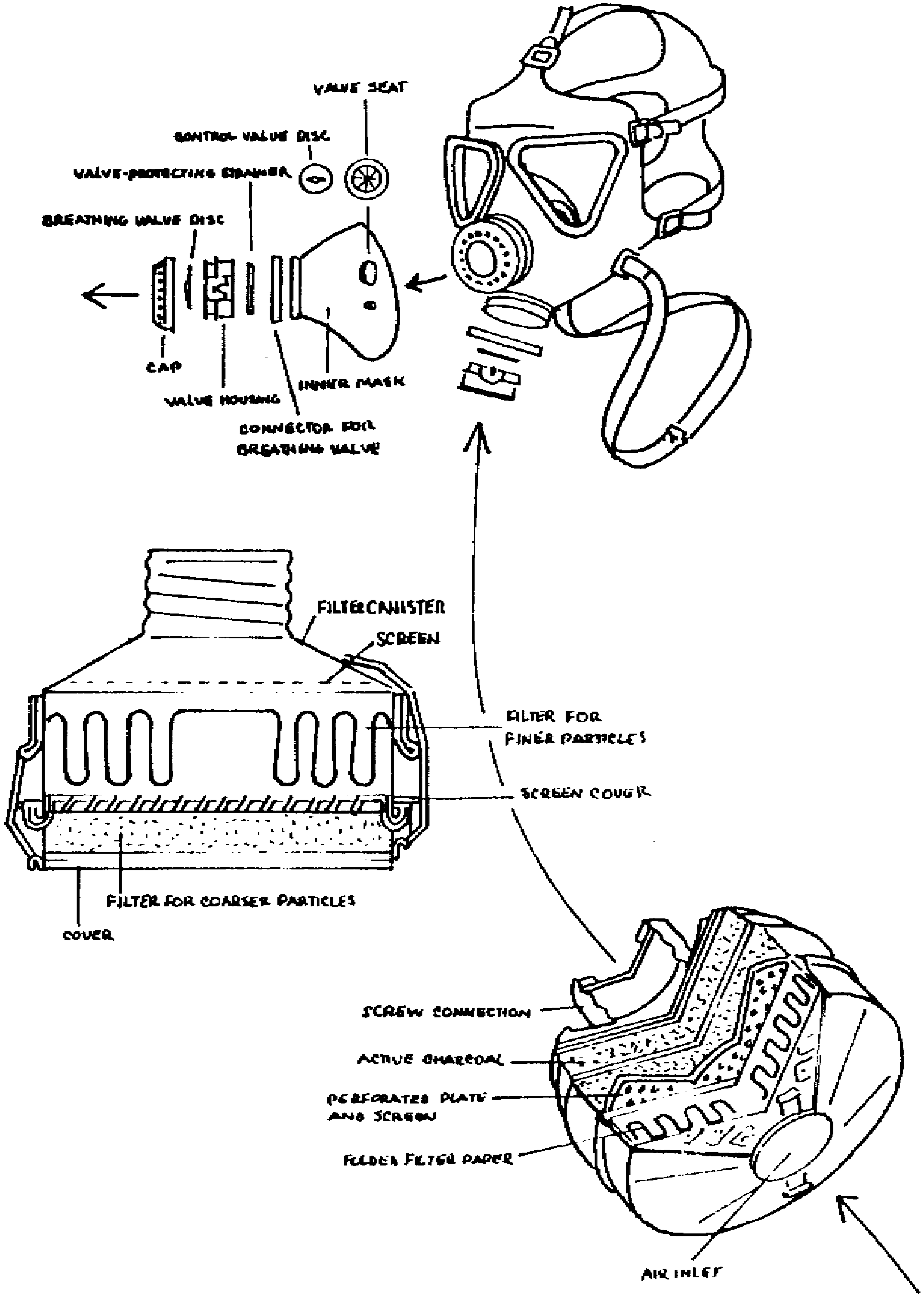
GRADE CODE: 1-SLIGHT, 2-MODERATE, 3-SEVERE, P-PRESENT

When the tests results have been recorded, the government requires the following warning statements to be included with labeling of containers with the tested chemical. These results serve as an excellent guide for choosing potential inhalation weapons or improvising them in the field.

Toxicity Category	Signal Word	Precautionary Statements
1 LC50 up to and including 0.05 mg/l (4 hour exposure)	Danger	Fatal if Inhaled. Do not breathe dust, (vapor or mist). Identify the correct, specific respiratory device approved by OSHA and/or MSHA
2 LC50> .05-.5 mg/l chamber concentration for 4 hours	Warning	May be fatal if Inhaled. Do not breathe dust (vapor or mist). Wear a mask or pesticide respirator approved by OSHA or MSHA
3 LC50> .5-5 mg/l chamber concentration for 4 hours	Caution	Harmful if Inhaled. Avoid breathing dust, (vapor or mist).
4 LC50 > 5 mg/l concentration for 4 hours	None	None required

Any label which carries the signal word "Danger" and the precautionary statement "fatal if inhaled" is an effective poison gas.

To protect yourself against this type of hazard, it is necessary to provide complete protection against contact and exposure around the mouth and nose. All the air must be filtered by a dust mask if the chemical is a solid or by a specific filter cannister on a gas mask that is known to work specifically for the chemical in question if it is a mist or vapor.


VALVE SEAT
CONTROL VALVE DISC
VALVE-PROTECTING STRAINER
BREATHING VALVE DISC
CAP
VALVE HOUSING
CONNECTOR FOR
BREATHING VALVE
INNER MASK
FILTER CANISTER
SCREEN
FILTER FOR
FINER PARTICLES
SCREEN COVER
FILTER FOR COARSER PARTICLES
COVER
SCREW CONNECTION
ACTIVE CHARCOAL
PERFORATED PLATE
AND SCREEN
FOLDED FILTER PAPER
AIR INLET

Military gas masks are designed with filter pads (six core layers laminated between two packing layers) composed of viscose rayon, vinyon, and glass fibers. The core layers are impregnated with 75% Whetlerite which is a finely ground activated carbon which has been immersed in a a solution of ammoniacal solution of silver, copper, chromium, and carbon dioxide. It is then dried at temperatures high enough to drive off ammonia from the resulting granules. This formula provides complete protection against all known military toxic chemical agents but does not protect against some industrial toxics like ammonia and carbon monoxide.

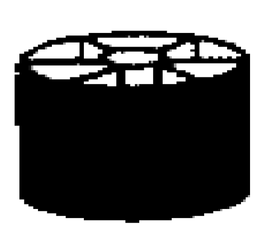
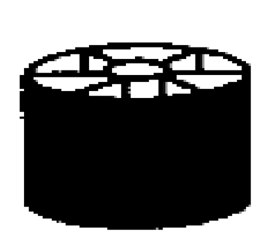
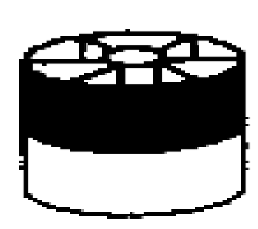
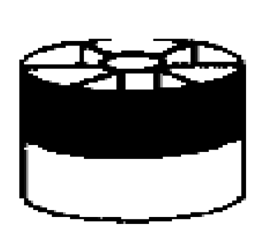
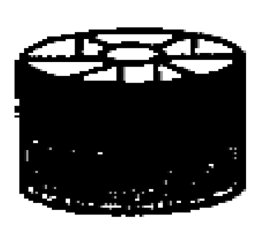
A few years ago, the developed a self foaming compound to deliver herbicides onto tree roots in sewer lines. We tested a number of candidates and mixed a few small batches containing powdered copper sulfate. This material was ground to a talcum powder consistency. When we mixed it into our foaming compound, the copper dust leaked out around our seal on the mixer. It then was sucked around the edges of the respirators and into the lungs of the workers. It became life threatening within seconds and we were lucky to have no fatalities. We removed the chemical from our list of candidate herbicides because it was too dangerous for our workers to handle in this fine of powdered form. At our feed mill a few blocks away, the granules of copper sulfate could be handled with complete safety and without dust masks. As you will learn in our chapter on solid chemical poisons, it is often the particle size and surface area of the material that makes it potentially lethal.

Fume respirator and gas mask cannisters usually use special materials for each chemical class they encounter. They are available from most safety supply companies. The filter generally contains a particulate layer as well as layers impregnated with chemicals to react with and neutralize the toxic air weapon in question. When the chemical in the mask is used up, it is possible for the air delivered poison to pass through the mask. This requires that the wearer of the mask will reach a safe area to remove and replace the filter cannisters periodically.

Improvised masks can be quickly made up using handkercheifs or other cloth soaked in solutions of activated finely ground charcoal and baking soda. This offers some temporary protection against many acids, bases and other toxic gases.





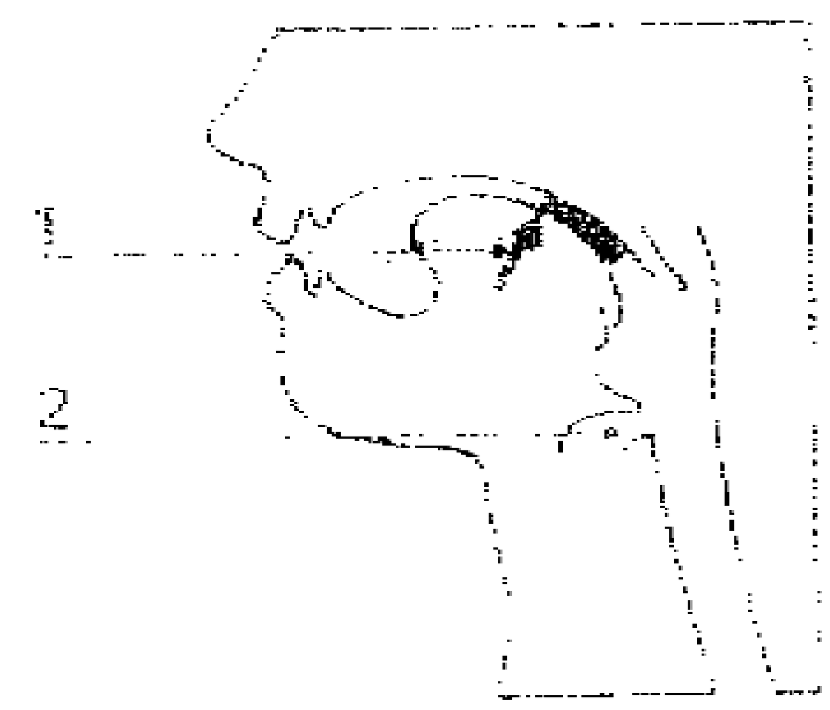
Cartridge/ Filter Type	Order No.	Description	Approved For	NIOSH/ MSHA
	7A-29943	GME Super Cartridge	Organic vapors, sulfur dioxide, chlorine, hydrogen chloride, chlorine dioxide, hydrogen fluoride, ammonia, methylamine, formaldehyde, pesticides, paints lacquers and enamels. Hydrogen sulfide for escape only.*	TC-23C-1582 TC-23C-1584
	7A-18808	Organic Vapors Cartridge	Organic vapors.*	TC-23C-40 TC-23C-144
	7A-18809	Acid Gases/Organic Vapors Cartridge	Organic vapors, chlorine dioxide, hydrogen chloride, sulfur dioxide. Hydrogen sulfide for escape only.*	TC-23C-47 TC-23C-146
	7A-18810	Acid Gases Cartridge	Chlorine, chlorine dioxide, hydrogen chloride, sulfur dioxide. Hydrogen sulfide for escape only.*	TC-23C-41 TC-23C-145
	7A-18811	Ammonia/ Methylamine Cartridge	Ammonia and Methylamine.*	TC-23C-43 TC-23C-147
	7A-18812	Formaldehyde Cartridge**	Formaldehyde, organic vapors and acid gases.*	TC-23C-917 TC-23C-921
	7A-18813	Mercury Vapor/ Chlorine Cartridge	Mercury vapor and chlorine.*	Not Approved
	7A-26654	High-Efficiency Dusts/Fumes/Mists Cartridge	Dusts, fumes and mists having a TWA less than 0.05 mg/m^3, asbestos-containing dusts and mists and radionuclides.*	TC-21C-135 TC-21C-155
	7A-29944	GME-H Super Cartridge/HEPA	Organic vapors, sulfur dioxide, chlorine, hydrogen chloride, chlorine dioxide, hydrogen sulfide (for escape only), hydrogen fluoride, ammonia, methylamine, formaldehyde, asbestos pesticides, paints lacquers, and enamels; dusts, fumes and mists having a TWA not less than 0.05 mg/m^3, asbestos-containing dusts and mists and radionuclides.*	TC-23C-1583 TC-23C-1585
	7A-18815	Organic Vapors/ HEPA Cartridge	Organic vapors, mists of paints, lacquers and enamels, pesticides, dusts, fumes and mists having a TWA less than 0.05 mg/m^3, asbestos-containing dusts and mists and radionuclides.* Not for use with urethane and other diisocyanate-containing paints.	TC-23C-161 TC-23C-155
	7A-18816	Organic Vapors/ Acid Gases/ HEPA Cartridge	Organic vapors, chlorine, chlorine dioxide, sulfur dioxide, dusts, fumes and mists having a TWA less than 0.05 mg/m^3, asbestos-containing dusts and mists and radionuclides. Hydrogen sulfide for escape only.*	TC-23C-159 TC-23C-153
	7A-18817	Acid Gases/ HEPA Cartridge	Chlorine, chlorine dioxide, sulfur dioxide, dusts, fumes and mists having a TWA less than 0.05 mg/m^3, asbestos-containing dusts and mists and radionuclides. Hydrogen sulfide for escape only.*	TC-23C-156 TC-23C-150
	7A-18818	Ammonia/ Methylamine/ HEPA Cartridge	Ammonia, methylamine, dusts, fumes and mists having a TWA less than 0.05 mg/m^3, asbestos-containing dusts and mists and radionuclides.*	TC-23C-158 TC-23C-152
	7A-18823	Pesticides/Organic Vapors Cartridge	Pesticides (not approved for fumigants), organic vapors, mists of paints, lacquers and enamels, dusts and mists having a TWA not less than 0.05 mg/m^3 or two million particles per cubic foot. Not for use with urethane or other diisocyanate-containing paints.*	TC-23C-79 TC-23C-148
	7A-18819	Dusts/Fumes/ Mists Filter	Dusts, fumes and mists having a TWA not less than 0.05 mg/m^3 or two million particles per cubic foot and radon daughters attached to dusts, fumes and mists as described above.*	TC-21C-134 TC-21C-187
	7A-18820 Cover 7A-18822	Aerosol Prefilter	Dusts and mists having a TWA not less than 0.05 mg/m^3 or two million particles per cubic foot. Filter covers required (sold separately).*	TC-21C-133 TC-21C-188
	7A-18824 Cover 7A-18825	Paint Spray Prefilter	Use with Organic Vapors Cartridge (sold separately) for protection against mists of paints, lacquers and enamels, dusts and mists having a TWA not less than 0.05 mg/m^3 or two million particles per cubic foot. Not for use with urethane or other diisocyanate-containing paints.*	TC-23C-80 TC-23C-149

** Do not exceed maximum use concentrations established by regulatory standards.*
*** OSHA regulations require that gas-proof goggles be worn with half-mask respirators when used for formaldehyde.*

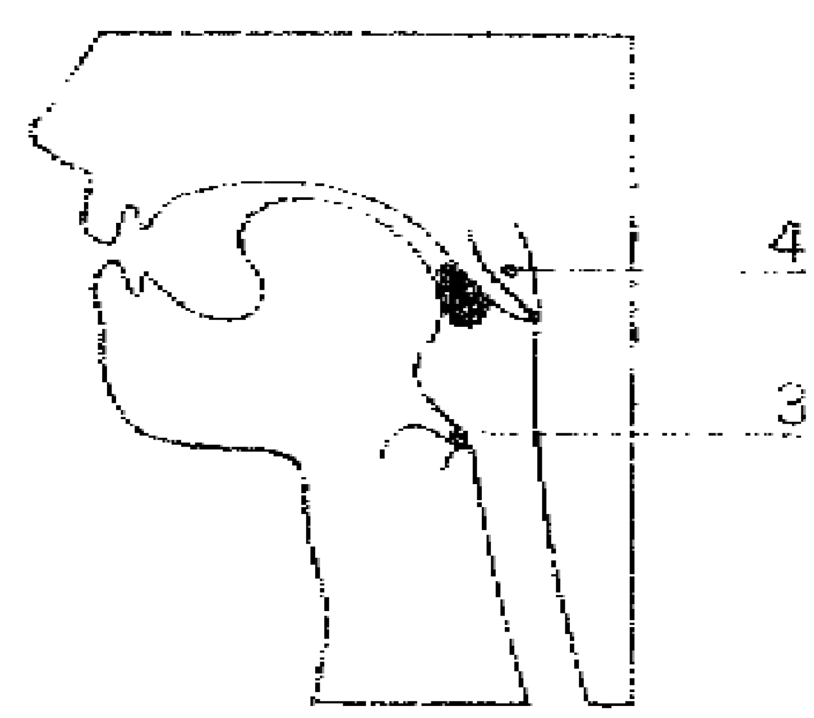
Ingestion Exposure

Poisons and anesthetics are used against food and water supplies of targeted populations and individuals so that they may be ingested while eating and drinking. The intent in war is to kill, injure and incapacitate, while chemicals that induce unconcousness are are used by kidnappers and rapists although military special forces have found occasion to use them as well to capture selected enemy individuals.

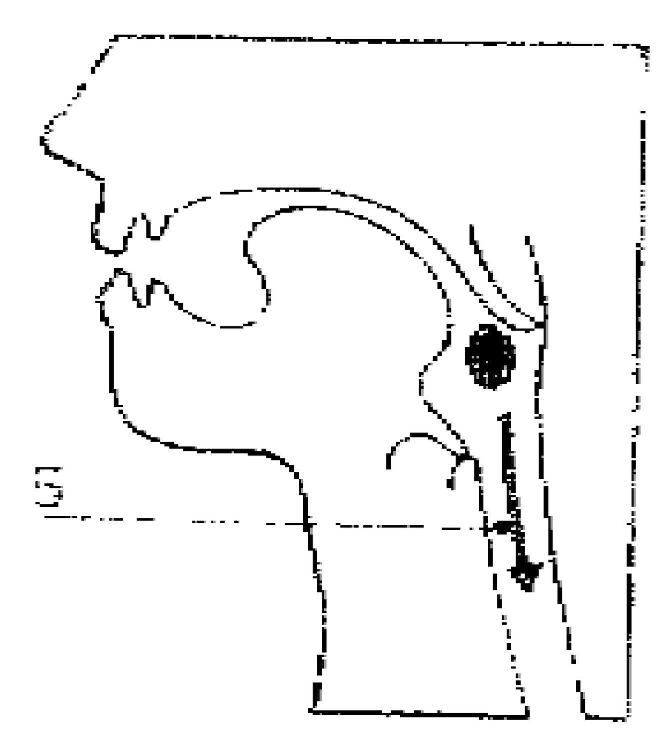
Ingestion begins by taking food or water into the mouth. Food is cut and ground by the teeth and mixed with saliva which softens the food and breaks down some of the carbohydrates.

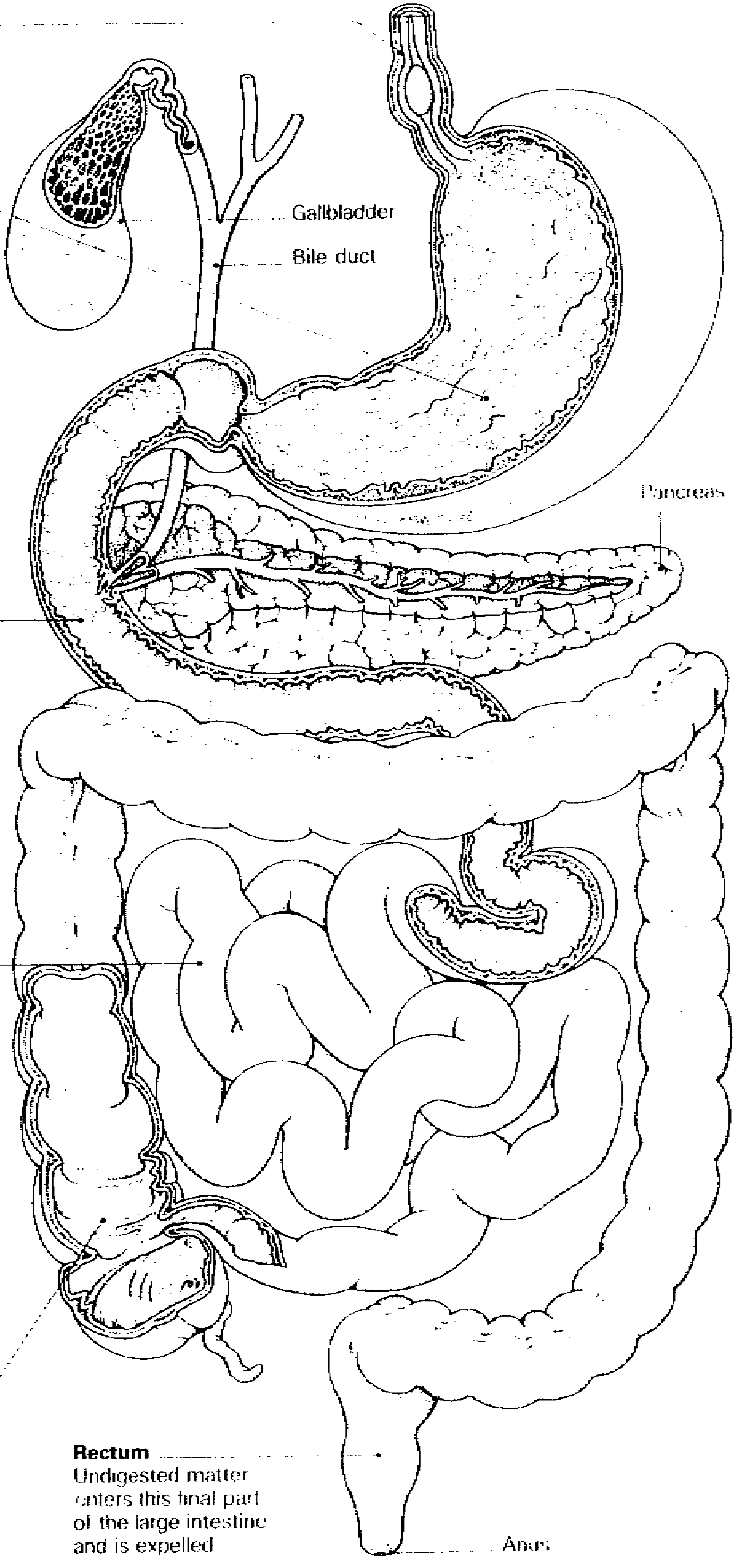


When we swallow, the tongue moves up and back (1) to push the food into the throat. The larynx rises (2) and the epiglottis drops down (3) to block off the trachea (windpipe). The false palate- the soft part of the mouths roof- moves back to block the airway to the nose (4). The food then travels down the esophagus (throat-5).



The chemistry of the particular poison determines where and how fast it is absorbed into the bodies tissues. Some poisons act in minutes while others take days. Some cause cancer and kill in years.





Esophagus
Food is carried down the esophagus by peristaltic action and enters the stomach.

Stomach
Food is broken down further by churning and by the action of hydrochloric acid and digestive enzymes secreted by the stomach lining. Food remains in the stomach until it is reduced to a semiliquid consistency (chyme), when it passes into the duodenum.

Duodenum
As food travels along the duodenum, it is broken down further by digestive enzymes from the liver, gallbladder, and pancreas. The duodenum leads directly into the small intestine.

Small intestine
Additional enzymes secreted by glands in the lining of the small intestine complete the digestive process. Nutrients are absorbed through the intestinal lining into the network of blood vessels and lymph vessels supplying the intestine. Undigested matter passes into the large intestine (the colon).

Colon
Water in the undigested matter leaving the small intestine is absorbed through the lining of the colon. The residue passes into the rectum.

Rectum
Undigested matter enters this final part of the large intestine and is expelled.

The digestive system is the group of organs that breaks down food into the tiny chemicals that the body can absorb and use for energy as well as building and repairing cells and tissues. The digestive tract is basically a tube through which food and water that we ingest will pass. The movement of this mix is accomplished by "peristalsis" which are waves of muscle contractions of the intestinal wall which push the mash along.

Foods supply vitamins, minerals, carbohydrates, proteins, and fats, as well as some water. The water, vitamins and water soluble minerals are absorbed directly into the bloodstream quickly and without change. Water soluble poisons such as basic minerals like arsenic and lead also pass directly into the bloodstream. Carbohydrates are broken down later by enzymes, acids, and salts into three simple forms of sugars called glucose, fructose, and galactose. Proteins are likewise broken down into polypeptides, peptides, and amino acids.

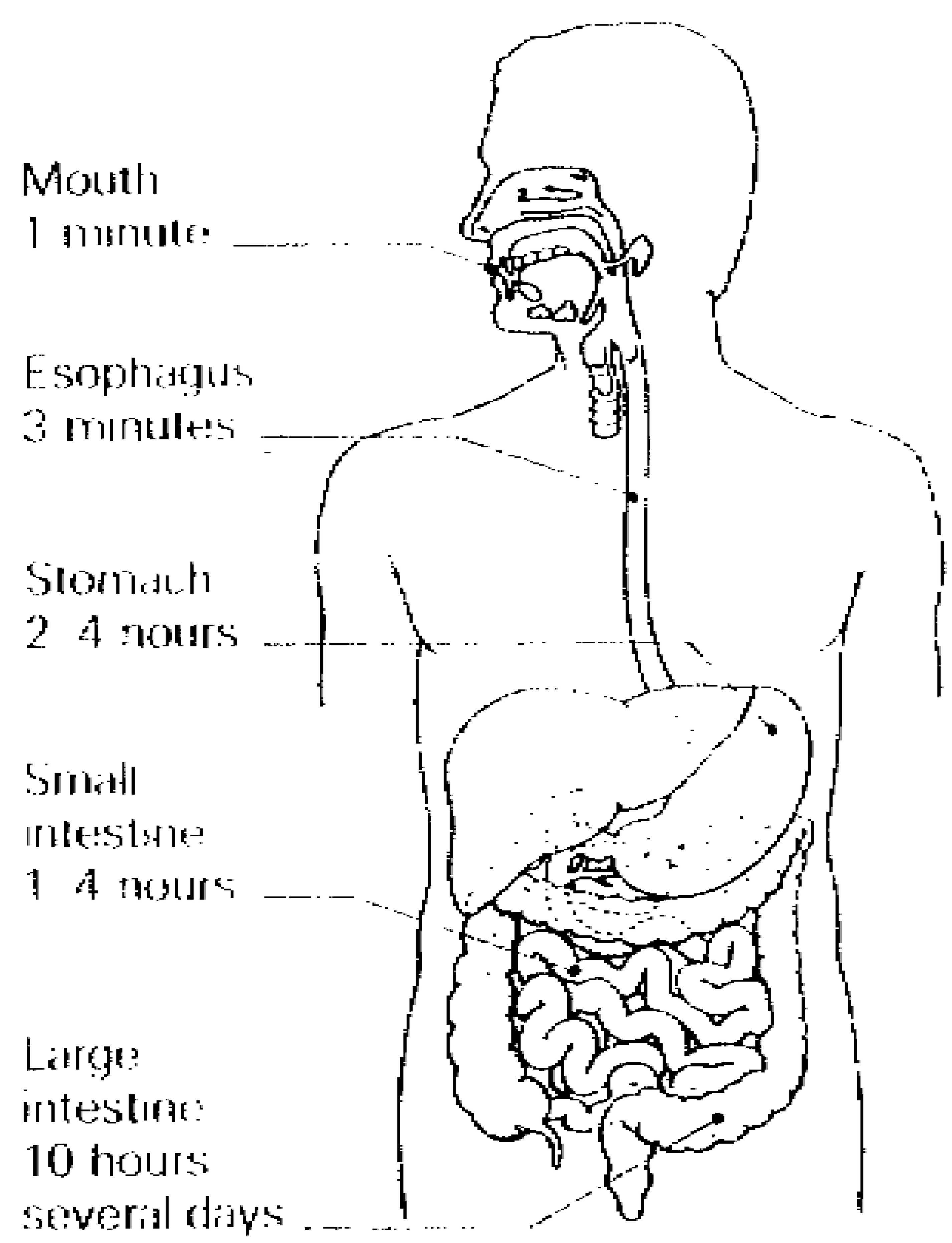
Bile salts and acids produced by the liver are stored in the gall bladder and added in the duodenum. Fats which are not broken down by the stomach acids are converted into fatty acids, glycerol, and glycerides here.

Most of these nutrients are absorbed in the small intestine where they pass through its thin lining into the bloodstream or lymphatic system.

Eventually, the remaining food passes into the large intestine where most of the water it contains is absorbed by the lining of the colon. Undigested material and sloughed off cells are then expelled by the rectum and anus as feces.

Chemicals can cause injury by directly damaging the cells lining the esophagus and stomach. This is what happens when acids or caustic materials are swallowed and is often fatal. All other chemicals will damage or disrupt the structure and/or function of cells. Toxins are poisonous proteins produced by other living organisms and will be covered in Volume 6-Bio Weapons.

The approximate period food spends in each part of the digestive system is shown below.



A number of common everyday exposures toxic chemicals occurs and we will mention a few here -

Arsenic can occur as organic salts and inorganic materials. Exposure to ore smelting, coal burning, and use of pesticides containing arsenic has resulted in lung and skin cancers, skin lesions, peripheral nerve effects, and cardiovascular changes. It is a favorite of deliberate poisoners (murderers) and when applied in large doses it directly affects the lining of the intestine, producing painful nausea, vomiting-sometimes with blood, diarrhea, excessive sweating, and burning of the throat. Collapse and death quickly follow. Chronic poisoning at lower doses is first noticed as weakness, fatigue, scaly skin, keratosis, and swelling of the lining of the mouth. Neuropathy then sets in producing tingling followed by numbness of the hands and feet. Dimercaprol is a drug that helps remove arsenic salts from the body.

Barium is a white silvery metal that acts like calcium and accumulates in the bones. It is used in rat poisons, paints, fireworks, and plastics. Once absorbed into the bloodstream it causes strong and prolonged contractions of all the bodies muscles including the digestive tract and heart. This results in violent bowel movements, vomiting, severe abdominal pain, excessive salivation, muscle twitching, elevation of blood pressure and accelerated heart activity. Muscular weakness follows with eventual paralysis of the limbs and respiratory muscles which can result in painful death. A fatal dose can be as little as one gram. Barium appears to act by altering the membranes in nerves and muscles preventing the in and out flow of potassium. Intravenous potassium will relieve most symptoms.

[This is a good example of how the basic chemistry rules apply. Barium resembles other metals used by the body but acts on it differently in a way that causes harm because it forms different kinds of bonds within the tissues]

Cadmium is a metal that accumulates in the soft tissues of the body. It depresses the immune system and causes irreversible kidney and liver disease. Ingestion of poisoned food or drink leads to vomiting, diarrhea, and shock followed by chest pain, coughing, chills, muscle aches, and nausea 4-10 hours after ingestion. Doses are fatal in hours to days. Cadmium is found in batteries and has been ground up into fine powder and used in deliberate poisonings.

Lead is a common metal that has found its way into human food and water supplies. Ancient Romans noticed that people died in uncommonly large numbers in the areas where lead pipes were used to transport drinking water. Lead behaves like calcium in the body and accumulates in bone tissues. Lead used in storage batteries, gasoline additives, ammunition, and solder has been implicated in accidental and deliberate poisonings. Lead poisoning that is gradual produces vague and nonspecific symptoms. It affects the production of blood cells, the nervous system, kidneys, reproductive system and kidneys. Irreversible brain damage occurs at concentrations of 100 PPM in blood.

Testing is done on rats to determine the amount required to kill 50% of the animals in a single dose. This dose is administered in what is called a gavage. This means that a dose is mixed into water and it is poured down the throat with a tube. The amount of dose is measured in grams or milligrams and weighed out as a percentage of the body weight of the animal. The rats are then observed for 14 days. The 5 female and 5 male rats are counted and if more than half live the dose is doubled for the next test. If less than half live it is cut in half. By this series of tests, it is possible to determine how much chemical is necessary to kill 50% of the animals. The animals are also examined to identify how the poison acted on them so that proper precautionary statements can be included with labeling about the chemical. This type of test is called an acute oral toxicity test.

Observations are made at 1 hour and then daily for the following -

(A) The skin and fur; *These were recorded at 1 hour, and daily thereafter for 14 days or until the rat died. These were recorded in Table A (males and females).*

(B) Eyes and mucous membranes; *These were recorded at 1 hour, and daily thereafter for 14 days or until the rat died. These were recorded in Table B (males and females).*

(C) Respiratory system; *These were recorded at 1 hour, and daily thereafter for 14 days or until the rat died. These were recorded in Table C (males and females).*

(D) Circulatory system; *These were recorded at 1 hour, and daily thereafter for 14 days or until the rat died. These were recorded in Table D (males and females).*

(E) Autonomic and central nervous system; *These were recorded at 1 hour, and daily thereafter for 14 days or until the rat died. These were recorded in Table E (males and females).*

(F) Somatomotor activity; *These were recorded at 1 hour, and daily thereafter for 14 days or until the rat died. These were recorded in Table F (males and females).*

(G) Behavior pattern. *These were recorded at 1 hour, and daily thereafter for 14 days or until the rat died. These were recorded in Table G (males and females).*

(H) Particular attention should be directed to observation of tremors, convulsions, salivation, diarrhea, lethargy, sleep and coma.

An example of the autopsy (gross necropsy) is given here as an example of the evaluation given to animals killed by poisons during testing. This information is readily available on nearly all of the 10 million substances that are known to exist and provide a wealth of data on candidate chemicals for use in small and large scale chemical warfare. Those canididates best suited for water and food supply targets are most effective in producing low LD50's in ingestion hazard testing.

Gross Necropsy: ***Rat*** FEMALE ***#1*** Dose Level ***5000 mg/kg***

===

Date of death: 08-08-90 (Day 0) Time 14:25 {015 minutes}

ANIMAL ID: *FEMALE* #1 Weight at necropsy: 42 g

Findings:

Foam was present around the mouth. The tongue, gums, and footpads were cyanotic. Upon entrance into the thoracic cavity the middle lobe of the left lung was brownish-green and all but the dorsal aspect of the right cranial lung lobe, were congested. No froth or fluid was present in the trachea. No other gross lesions were observed.

Diagnosis: Aspiration pneumonia.

Date of death: 08-09-90 (Day 0) Time: 07:00 = 17 hours

ANIMAL ID: *MALE* # 1 Weight at necropsy: 29 g

Findings:

Dried hemorrhagic froth was present around the mouth and external nares and was also found to be adhered to the dorsal surface of the tongue. Upon opening the abdominal cavity it was observed that the stomach had a hole along the greater curvature and appeared to have ruptured as coffee colored stomach contents were along that area and throughout the peritoneal cavity. Pale areas on the edges and caudal dorsal surfaces of of the right and left medial lobes of the liver were noted as well. No other gross lesions were observeable.

Diagnosis: Hemorrhagic gastritis with concurrent rupture and peritonitis.

A table summarizing the mortality rates is given to illustrate how the LD50's are calculated.

Table 1. Rat, sex, dose weights at 0, 7 & 14 days and mortality.

Rat	Sex	Dose Mg/Kg	Start Grams	Dose mg	Dose ml	1-Hr Status	24-Hr Status	7-Day Status	14-Day Status	7-Day Grams	7-Day ADG	14-Day Grams	14-Day ADG	14-Day Gain	14-Day AVG
1	Ma A	5000	26	130	0.52	Alive	Dead	Dead	Dead	Dead	Dead	Dead	Dead	Dead	
2	Ma A	5000	42	210	0.84	Alive	Dead	Dead	Dead	Dead	Dead	Dead	Dead	Dead	
3	Ma A	5000	32	160	0.64	Alive	Dead	Dead	Dead	Dead	Dead	Dead	Dead	Dead	
4	Ma A	5000	39	195	0.78	Alive	Dead	Dead	Dead	Dead	Dead	Dead	Dead	Dead	All
5	Ma A	5000	41	205	0.82	Alive	Alive	Dead	Dead	Dead	Dead	Dead	Dead	Dead	Dead
6	Ma B	2500	39	98	0.78	Alive	Alive	Alive	Alive	62	3.3	134	6.79	95	
7	Ma B	2500	44	110	0.88	Alive	Alive	Alive	Alive	86	6.0	132	6.29	88	
8	Ma B	2500	31	78	0.62	Alive	Alive	Alive	Alive	70	5.6	107	5.43	76	
9	Ma B	2500	27	68	0.54	Alive	Alive	Dead	Dead	Dead	Dead	Dead	Dead	Dead	
10	Ma B	2500	47	118	0.94	Alive	Alive	Alive	Alive	114	9.6	148	7.21	101	90.0
11	Ma C	1250	45	56	0.90	Alive	Alive	Alive	Alive	95	7.1	149	7.43	104	
12	Ma C	1250	31	39	0.62	Alive	Alive	Alive	Alive	84	7.6	125	6.71	94	
13	Ma C	1250	39	49	0.78	Alive	Dead	Dead	Dead	Dead	Dead	Dead	Dead	Dead	
14	Ma C	1250	43	54	0.86	Alive	Dead	Dead	Dead	Dead	Dead	Dead	Dead	Dead	
15	Ma C	1250	34	43	0.68	Alive	Alive	Dead	Dead	Dead	Dead	Dead	Dead	Dead	99.0
16	Ma D	625	46	29	0.92	Alive	Alive	Alive	Alive	99	7.6	163	8.36	117	
17	Ma D	625	27	17	0.54	Alive	Alive	Alive	Alive	57	4.3	109	5.86	82	
18	Ma D	625	33	21	0.66	Alive	Alive	Alive	Alive	67	4.9	110	5.50	77	
19	Ma D	625	38	24	0.76	Alive	Alive	Alive	Alive	83	6.4	132	6.71	94	
20	Ma D	625	43	27	0.86	Alive	Alive	Alive	Alive	90	6.7	146	7.36	103	94.6
		5000	36.0	Total	3.6	0/5	4/5	5/5	5/5	Dead	Dead	Dead	Dead	Dead	
		2500	37.6	Total	3.8	0/5	0/5	1/5	1/5	83.0	6.1	130.3	6.4	90.0	n = 4
		1250	38.4	Total	3.8	0/5	1/5	3/5	3/5	89.5	7.4	137.0	7.1	99.0	n = 2
		625	37.4	Total	3.7	0/5	0/5	0/5	0/5	79.2	6.0	132.0	6.8	94.6	n = 5
							LD50 =	1539	1539						
				Upper 95% Confidence Interval =				2487	2487						
				Lower 95% Confidence Interval =				952	952						

Once the LD50 is known and the mode of action in the cause of death is understood, a set of precautionary statements is added to the labeling according to the following government regulations.

Toxicity Category	Signal Word	Precautionary Statement
1 LD50 up to and including 59 mg/kg body weight	Danger	Fatal if Swallowed. Wash thoroughly with soap and water after handling and before eating or drinking
2 LD50>50 to 500 mg/kg body weight	Warning	May be fatal if swallowed. Wash thoroughly after handling and before eating or drinking
3 LD50>500 to 5,000 mg/kg body weight	Caution	Harmful if swallowed. Wash thoroughly with soap and water after handling.
4 LD50> 5,000 mg/kg body weight	None	None

Those chemicals labeled as fatal if swallowed are the most effective candidates for poisoning food and water supplies because they can kill at the smallest doses possible.

The only measures that can be taken to protect against this type of threat are

1. Protect the food and water supplies against direct delivery of poisons into the food and water chain.

2. Wash after handling anything that leaves dust on the hands or eating utensils.

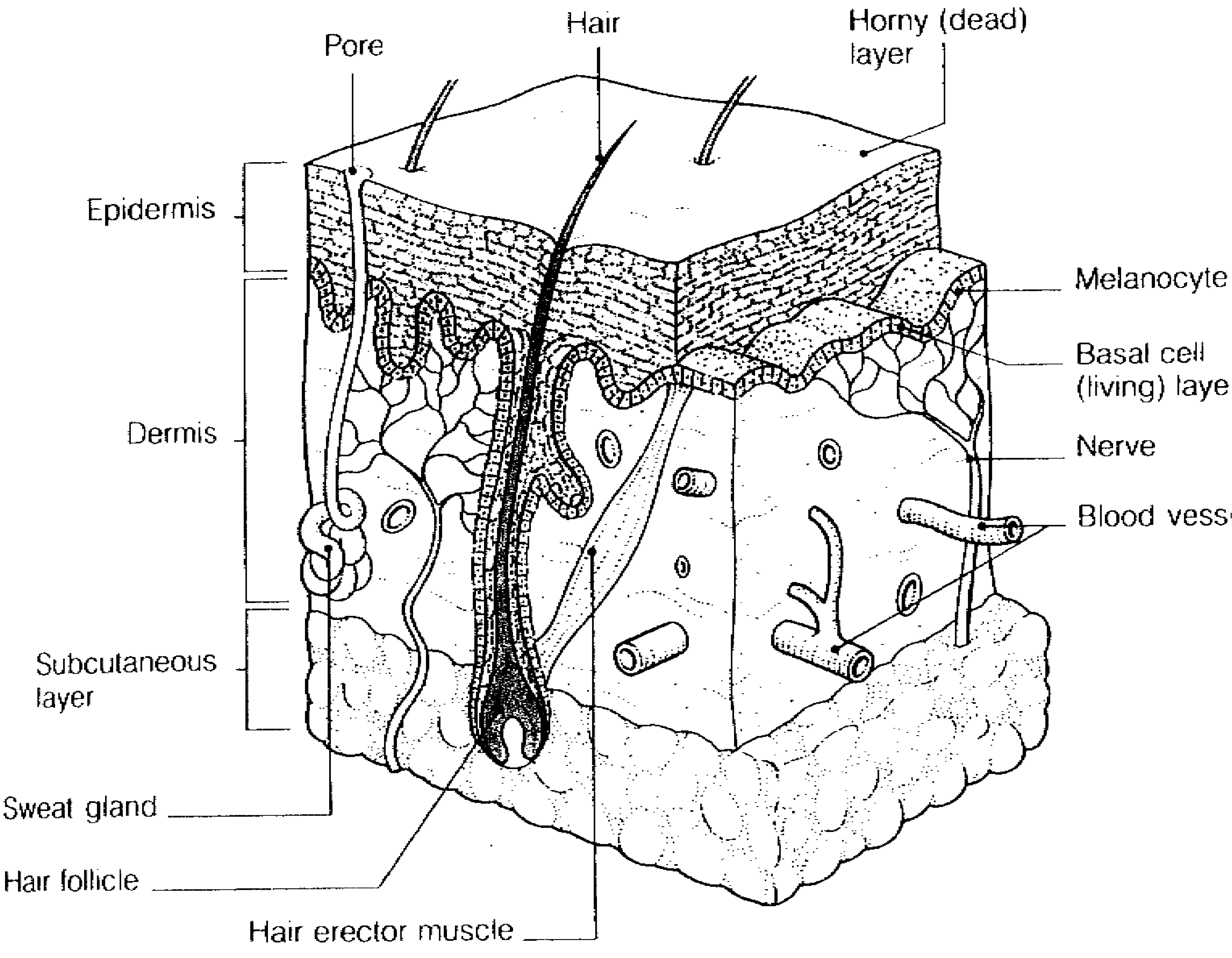
3. Boil, and if possible, distill all drinking water. This can also be required for any water that may be used to wash dishes so that poisonous residues do not remain on eating utensils from contaminated water.

4. Food should be examined for entry points of contamination and washed thoroughly. If there is doubt to its safety it can be tested on animals first or simply avoided. The survival section in Volume 2, chapter 11 describes procedures for sampling questional food in the wild.

To give an idea of just how small a dose that "fatal if swallowed" means, you can take the 59 milligrams per kilogram and calculate it out for a 200# man. You divide the 200# by one million and multiply by 60 to get the weight necessary to kill him. This is about .012 pounds or 5 grams. This amount can fit under a single fingernail.

Dermal Exposure

Many chemicals can harm or kill by damaging, destroying, or passing through the skin. The skin is made up of two main parts, the "Epidermis" is the outside protective layer which contains disposable dead cells for its outer layer or covering. The "dermis" (true skin) lies underneath and contains most of the living elements. Below the skin layer lies the main body tissues and circulatory system which moves all the nutrients around.



The skin is the largest organ of the body and protects the internal organs from the environment. The skin loses dead cells constantly to wear and tear and these are continually being replaced as new skin grows underneath.

The outer layer Epidermis is made up of flat cells that resemble paving stones when examined under a microscope. It is thickest on the body parts that are used the most in contact with the solids in the environment, such as the soles of the hands and feet. It is very thin in the eyelids and allow some light to pass and is generally thinner in women than men. The skin also thins with age.

The outer part of the epidermis is made up of the dead cells that form the tough, horny, protective coating. As these cells are worn away they are replaced by rapidly dividing living cells in the innermost part of the epidermis. In between is a transition region that is made up of both living and dead cells. Some of the cells produce the protective pigment melanin which gives us our skin color. At the base the cells grow flatter and fill up with keratin (which also makes hair and nails) and die. The dead cells form in stacks about 30 cells thick.

The Dermis is made up of connective tissue mixed into other specialized structures like the hair follicles, sweat glands, and the sebaceous glands that produce an oily substance called sebum which is made up of fats and wax. It lubricates the skin, keeps it supple, and prevents it from becoming sodden when we are swimming or bathing, and keeps it from drying out in dry climates. It also helps seal the skin surfaces to keep out bacteria, viruses, fungi, and tiny particulates. The dermis also contains blood and lymph vessels and nerves.

The skins most important function is to protect us by shielding our tissues from abrasion, harmful sunlight, invasion from harmful organisms, and chemicals. The skin is also a sensory organ and contains many cells that are sensitive to pain, pressure, and itching. It also helps keep our body temperature constant. When we are hot the sweat glands release water that cools our bodies down, and the blood vessels in the dermis dilate to help let the air cool the blood that is circulating. When we get cold, the skin constricts to hold in heat. Sweat glands close up and the hairs grow erect to produce a layer of still air that insulates the skin.

The epidermis contains enough sebum to make our skin waterproof so that we can swim or bathe without soaking up water like a sponge. The outer epidermis also can hold some water which helps make it elastic. If this water content drops below a certain level our skin cracks, which reduces its efficiency as a barrier. Our bodies are made up of 60% water and its stops most of it from evaporating away.

The skin can be injured through cuts, bites, radiation from the sun or other sources, burns, and chemicals. The skin also releases an antiseptic liquid from glands that help to heal wounds. The skin is usually about 1/16th of an inch thick but can be 1/8th" thick on foot soles and palms. As the body ages, the body bulk shrinks and the skin loses its elasticity causing bagginess and wrinkles.

Many common chemicals attack, harm, or pass through the skin. Some examples include -

Ammonia and all other caustic bases or alkalis. These cause direct inflammation and burns on the skin when present in concentration and mixing into the skin moisture. If the concentration is high enough, blisters form with second degree burns. With caustic soda, the skin fats and proteins are dissolved and the cells underneath continue to disintegrate with contact. Concentrations as low as .12% for an hour can cause injuries.

Creosote is a wood preservative used on railroad ties, construction lumber, and utility poles. Contact with its vapors cause progressive burning, itching, discoloration, ulceration of the skin, and , ultimately, gangrene.

Dioxane, found in Holcombs window cleaner and in other chemical mixtures under various names (see volume 1) is readily absorbed through the skin with delay of onset of toxic symptoms. It easily passes through the skin and large doses may kill. It produces intoxication, narcosis, pulmonary edema, kidney and liver damage, and death.

Acids of all types directly attack, react with, dissolve, and destroy skin tissues on contact. The rate is greatly accelerated if the acid is boiling. In a research experiment to produce a dry acid version of sulfuric acid, the author accidentally spilled a few drops on his hand and arms. The burns were instant and the pain was excrutiating. When I was about 12 years old, I had a fingernail yanked out by a tractor clutch and this had been the most painful moment in memory until the boiling acid experience. The pain took about 24 hours to subside to tolerable levels even with painkillers.

Even mild solid acids like oxalic acid are caustic to the skin. Cracking and fissuring of the skin and development of slow healing ulcers are common with substantial contact. Military preparations of nerve gas shells often contain acids or other blistering agents to help destroy skin tissues since the absorption rate improves drastically once the 30 or so dead outer layers are out of the way.

The blood supply to the skin is one of the richest in the body. Whatever passes through the skin ends up being absorbed into the bloodstream readily. The bloodstream then rapidly transports it throughout the body which is why nerve agents work so fast. When common solvents are spilled onto the skin, they are absorbed so quickly that traces are found in the urinary track in as little as 20-30 minutes.

Dry and powdery chemicals are absorbed more slowly through the skin. Water based chemicals are much more dangerous as they help speed the passage of chemicals up to 10 times as fast as dry substances. Oils will permit absorption faster than water. Injuries such as cuts or burns also drastically speed movement of chemicals into the body. Some chemicals like DMSO (Dimethyl Sulf Oxide) open pores in the skin so that larger molecules of chemicals can pass more quickly. Solvents strip skin cells of vital oils and fats which speeds chemical absorption. All these are important considerations in preparing or defending against chemical weapons intended for dermal attack.

To test for dermal toxicity, 5 male and 5 female rabbits have fur clipped from 10% of their body surface. The poison is normally applied on the dorsal and ventral areas in the form it is used in the field. A thin and uniform film of the chemical is applied over the entire clipped surface of exposed skin and left in place for 4 hours. The animals are restrained to prevent licking or rubbing any of the chemical off. The effects are observed and recorded and any unusual toxic effects are evaluated with the animals studied to determine which tissue damage is related to the cause of death.

In the case of liquids and gases the material is often made into a paste to insure adhesion to the skin. Oil may be used to facilitate adhesion and absorption of the substance. Variations of the dose and area covered can be used to adjust for extreme toxicity. Most injuries related to small doses are recorded as edema and erythema formation with descriptions of the nature and the reversibility of corrosion or irritation.

The following are observed and recorded-

- Behavioral effects
- Skin and fur changes and reversibility
- Gross Lesions
- Mortality
- Eyes and mucous membranes
- Respiratory System
- Circulatory System
- Autonomic and central nervous system
- Somatomotor activity
  - Tremors
  - Convulsions
  - Salivation
  - Lethargy
  - Sleep
  - Coma

Weight gain or loss

An example of simple skin scoring is provided here.

Edema Formation

No edema	0
Very slight edema (barely perceptible)	1
Slight edema (edges of area well defined by definite raising).	2
Moderate edema (raised approximately 1 millimeter)	3
Severe edema (raised more than 1 millimeter and extending beyond area of exposure)..	4
Maximum possible	4

Table 1a. Erythema and edema scores for 10 rabbits (5 females and 5 males)
Compound: Scores at 24, 48, 72, 96, 120, 144 and 168 hours.

Rabbit	Sex	S.F.C. Treatment	Wt. kg	S.F.C. Grams	24 Hrs Eryth	24 Hrs Edema	48 Hrs Eryth	48 Hrs Edema	72 Hrs Eryth	72 Hrs Edema	96 Hrs Eryth	96 Hrs Edema
93	M	Treated	3.5	7	4	2	4	1	4	0	4	0
94	M	Treated	3	6	3	1	3	0	2	0	2	0
96	M	Treated	3	6	2	0	1	0	0	0	0	0
97	M	Treated	3	6	1	0	0	0	0	0	0	0
98	M	Treated	3.5	7	2	0	1	0	0	0	0	0
99	F	Treated	3	6	4	1	3	0	3	0	2	0
102	F	Treated	3	6	4	2	4	0	3	0	3	0
103	F	Treated	3.5	7	2	0	1	0	0	0	0	0
104	F	Treated	3	6	4	2	2	0	1	0	1	0
106	F	Treated	3	6	3	1	2	0	2	0	1	0
Mean Males			3.20		2.40	0.60	1.80	0.20	1.20	0.00	1.20	0.00
Std Dev Males			0.245		1.020	0.800	1.470	0.400	1.600	0.000	1.600	0.000

The amount necessary to kill the 50% of the animals through dermal exposure is determined and recorded. When this value is know, the following information is provided on labeling for the chemical.

Toxicity Category	Signal Word	Precautionary Statements
I LD50 up to and including 200 mg/kg of body weight	Danger	Fatal if absorbed through skin. Do not get in eyes, on skin, or on clothing. Wear protective clothing and rubber gloves. Wash thoroughly after handling with soap and water and before eating or drinking.
2 LD50>200 to 2,000 mg/kg of body weight	Warning	May be fatal if absorbed through skin. Do not get in eyes, on skin, or on clothing. Wear protective clothing and rubber gloves. Wash thoroughly with soap and water after handling and before eating or drinking.
3 LD50>2,000 to 5,000 mg/kg of body weight	Caution	Harmful if absorbed through the skin. Avoid contact with skin, eyes, or clothing. Wash thoroughly with soap and water after handling.
4 LD50>5,000 mg/kg of body weight	None	None

Those materials labeled "fatal if absorbed through skin" are the best candidates for use in dermal based vapor, mist, and dust weapons.

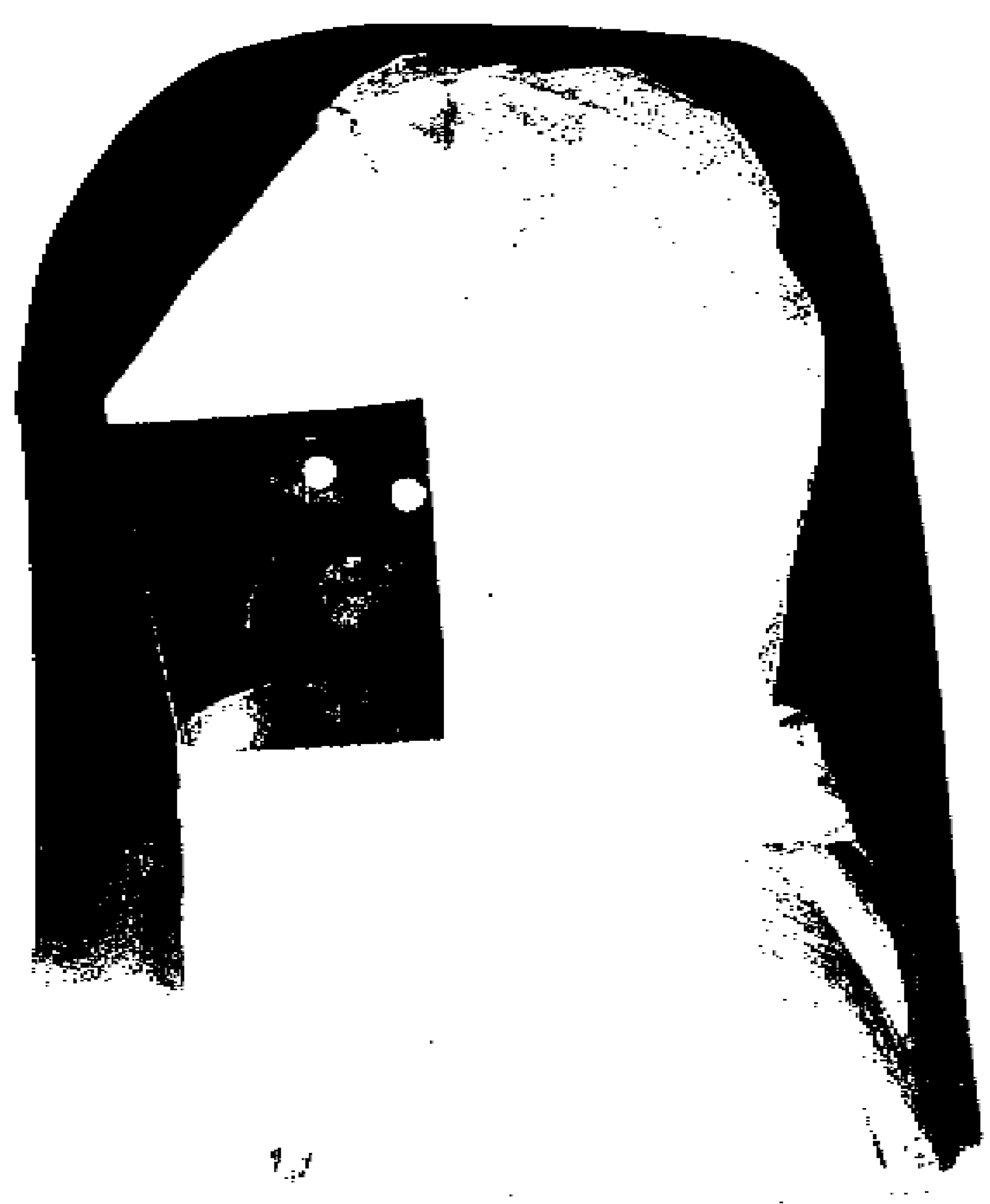
Defending against dermal or full body exposure attacks has been covered in Volume 2. We will cover some of the basic methods and materials used for defense here as well.

The entire body needs to be covered to protect against exposure to toxic compounds that kill on contact with skin surfaces. Airtight, impermeable clothing has been developed for both the military and industry to offer this type of protection. The clothing is usually made of butyl rubber or a coated fabric. Because this material does not breathe, it becomes hot and uncomfortable quickly. It retards the release of moisture and heat and personnel effeciency is lowered drastically if the suits have to worn for very long. Liquid contamination on the suits must be neutralized or removed before taking the suit off.

Some of the newer suits are impregnated with chemical to neutralize blister agents and still allow the wearer some comfort because the material will breathe. It is effective against vapors and mists but not against splashes of these agents. The outside of the fabric is treated with repellants to repel liquids and an inner layer of charcoal impregnated foam/nylon tricot laminate which absorbs chemical agent that pierces the outer layers.

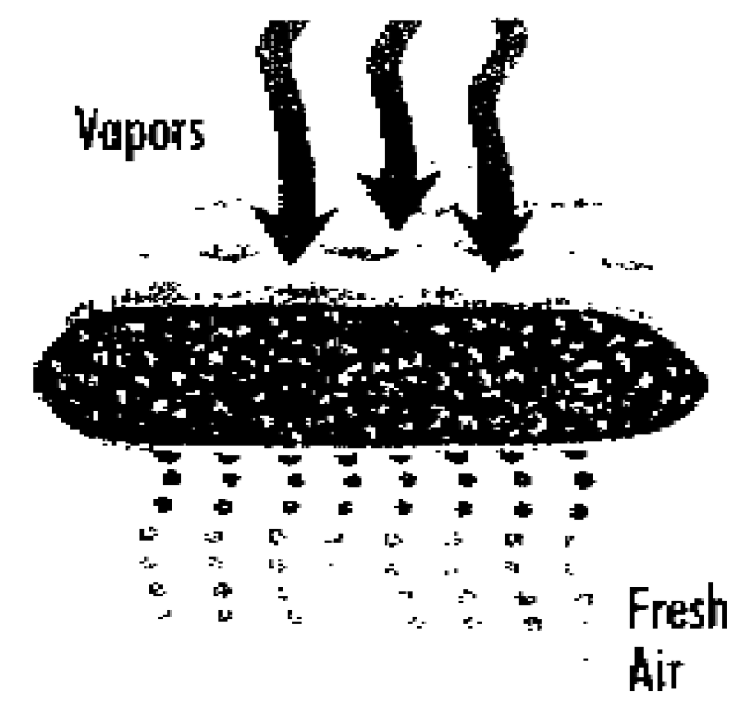
One of the best ideas illustrated in the hood below is a positive air flow suit in which air is pumped from a safe, filtered location into the suit to force outward all possible chemicals. This is the ideal situation for vehicles and rooms as well.

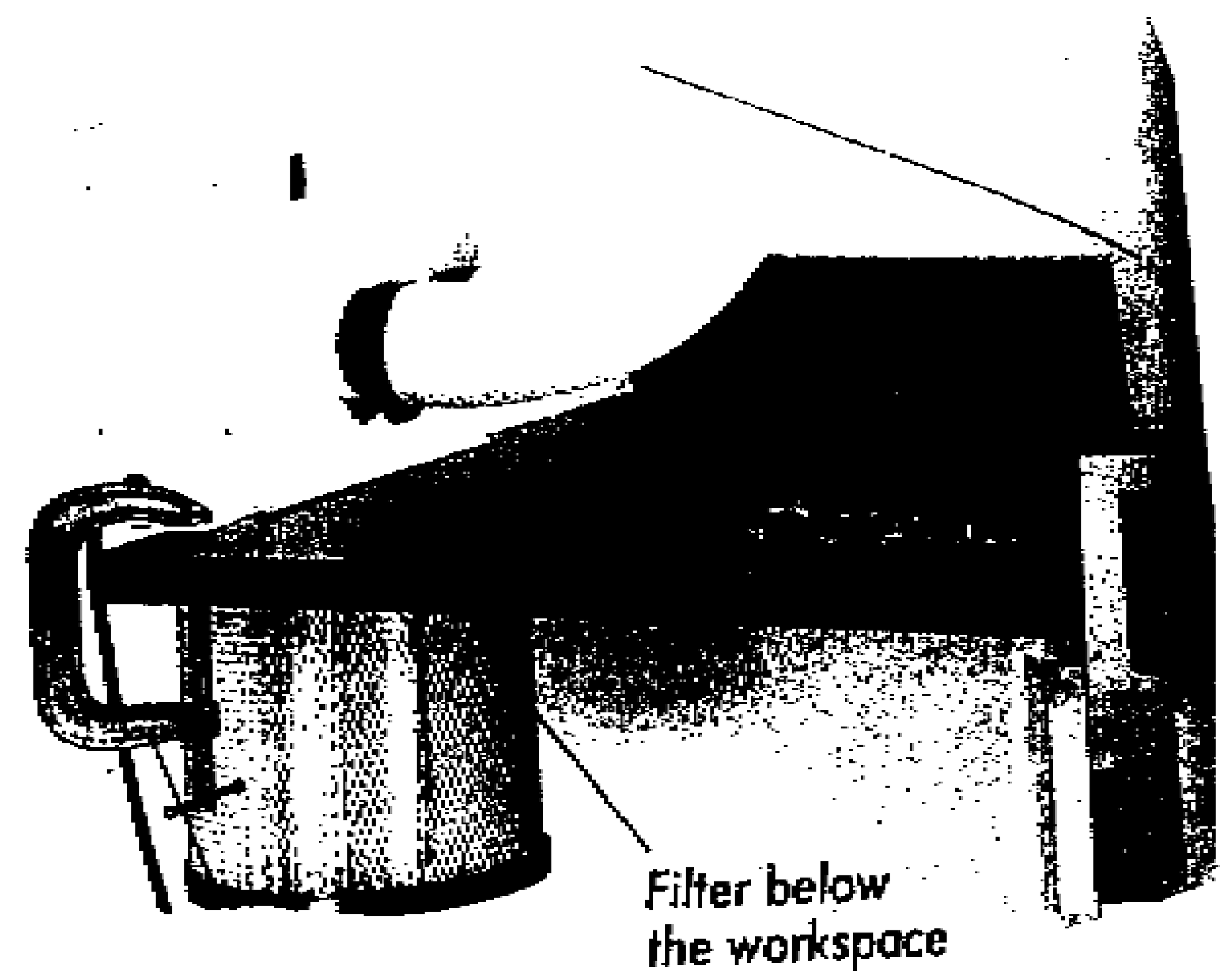




Small shelters must be available with positive, filtered airflow and ideally with diffusion board or plastic/charcoal impregnated liners. These air systems act like great big gas masks with the air forced through with a fan. Portable systems like this are available commercially from safety supply companies. A shower area is also necessary for decontamination.







Chapter 3

Non Phosphorus Military Chemical Weapons

There are over 10 million compounds known, nearly all of which are toxic in one way or another to human, animal, or plant life. Prior to WW1, there was no large scale attempt made to incorporate chemicals into regular use in war. There were two reasons for this.

1. A good understanding of chemicals and of the table of elements and how they work was not known until the latter part of the 19th century.

2. Once an understanding of chemicals was known, many new chemicals could be mass produced and sold. This led to the development of massive chemical industries. At the same time it led to the realization that toxic or incapacitating chemicals could substitute economically for bullets and bombs. If you had manufacturing plants that could make poison gas from the raw materials used in dyes, coal tars, and basic industries, you could substitute it for explosives and bullets when your ordnance ran low.

This last item is exactly what happened to the Germans in the winter of 1914-1915. They had depleted their stocks of explosives to the point of nearly running out. Without the great breakthrough the generals had promised, they now were stuck with a long trench battle line and few prospects of holding out as the chemicals used in producing explosives ran out. What Germany did have was a well developed and massive chemical industry and a lot of trained scientists who knew how to convert the raw materials for these industries into deadly chemical weapons. Out of a need to be able to continue the war, the Germans became the first nation in history to resort to large scale, organized chemical warfare.

Their scientists studied some 3,000 toxic materials for use in WW1. Most of the deadliest ones available were not used because of the many problems described in the last chapter that had to be overcome before the military could use them. About 30 chemical weapons were developed and used by both sides during WW1. Since WW1 many other chemical agents have been created.

In this chapter we are going to describe the military chemical weapons used in WW1 and those developed since then. In the 1930's and 40's, German and British scientists developed a completely new class of military chemical weapons called nerve agents. All these acted on the nervous system and were built around organophosphate molecules. These will be covered in depth in the next chapter because the phosphate chemistry involved in their manufacture is complex.

In the following chapters, we will cover hundreds of other known compounds that are as deadly or deadlier than the military poison chemical weapons, but could not be adopted for military use for one reason or another. In the last chapter we will cover in detail the science of constructing chemical weapons that can be delivered against enemy targets in a variety of ways and will teach the sciences of their use that distinguish them from projectile and explosive weapons.

In ancient times, armies would sometimes use poisoned spear and arrow tips in combat. Some armies as recent as the 1600's provided opium prior to battle which had the effect of rendering their soldiers insensible to the dangers they faced. The soldiers would throw themselves into combat "like wild beasts", knowing no retreat as long as their leaders held their posts. In all these centuries, no organized political or military state had built factories or institutionalized the manufacture of chemicals for use as weapons of war. On April 22nd, 1915, that all changed.

French and Canadian troops on the front lines at Langemarck noticed a curious green mist approaching them. They began to choke and gasp and many could barely escape the fog which had engulfed them. The Germans produced a small gap in the allies lines, which although serious, was not disastrous. All the allied nations were horrified and regarded this new weapons use as a crime against humanity that would never be forgotten.

On the German side, this first use of gas was an experiment, released from cylinders, it was concentrated on a front 600 yards wide once the prevailing winds were favorable. The gas they used was chlorine, and it effectively breached the lines. The Germans were unprepared to fully exploit it and British chemists soon produced a temporary respirator to protect the men from it.

In May and June 1915, the wind was generally blowing against the Germans which prevented them from initiating large scale attacks for fear that the gas would blow back directly on themselves. On Dec. 15th, 1915 the Germans launched a large scale gas attack across a three and a half mile front continuously for about an hour. The Chlorine gas now had little effect on the allies. This failure led the Germans to develop and produce a new weapon that they mixed with chlorine. Eighty eight tons were released from 4,000 cylinders on Dec 19th, 1915 with good effects, and in August 1916, the Germans launched a highly concentrated attack on a hot day with "Phosgene" gas. The gas killed allied soldiers as far as nine miles behind the lines because the winds were blowing in their direction. These deadly vapors could pass through the gas mask used against the chlorine. To make matters worse, the phosgene did not produce the terrible irritation of chlorine. Its odor was not unpleasant, it smelled like new mown hay, and was hard to even identify in the air at times. It would be quickly adapted by the allies and would produce over 80% of all the gas fatalities in WW1. A British Lt. Colonel named Harrison quickly developed an effective gas helmet with a special filter that was soon effective against this threat.

The chemical weapons were quickly adapted to be delivered by artillery shell, mortar, and air dropped bombs. The Germans then developed "Diphenylchlorarsine" which would be fired in the first round artillery volleys where a small explosive would disseminate it. This had the irritating effect of causing the men to sneeze uncontrollably to the point where they could not wear their gas masks. This made them vulnerable to the main gas attacks.

In July 1917, the most terrible weapon to date was brought into use. Di-chlorethyl sulphide was used on a large scale against the Italians and led to the breakthrough at Caporetto. This new "Mustard Gas" not only produced terrible blistering wounds, it persisted on clothing, boots, soil, weapons parts, and everything else, enabling it to harm "persistently".

During WW1, the nations at war produced chemical weapons by the tons as follows -

	Lacrimators	Lung Injurants	Vesicants	Sternutators	Totals/Tons
Germany	2,900	48,000	10,000	7,200	68,100
Austria	245	5,000	0	0	5,245
France	800	34,000	2,140	15	36,955
England	1,800	23,335	500	0	25,735
United States	5	5,500	710	0	6,215
Italy	100	4,000	0	0	4,100
Russia	150	3,500	0	0	3,650

During WW1, 6,000 tons of lacrimators were used and produced no casualties, but were effective at incapacitating large numbers of soldiers. 6,500 Tons of Sternutators were used in battle and produced 20,000 casualties (650# of gas per casualty), 110,500 tons of lung injurants were used to inflict 876,853 casualties (230# per casualty), and 12,000 tons of vesicants would be used to cause 400,000 casualties (60# per casualty). It is clear that the vesicant Mustard Gas was by far the most effective weapon in the war, producing casualties at a much greater rate for the same weight of material than bullets, explosives, or other chemicals.

The classes of chemicals that were developed and used in WW1 with the individual chemicals are -

Lacrymators which cause intense, temporary pain by irritating the eyes and lacrymal ducts. Commonly called tear gas, these included both simple acting as well as toxic chemicals -

Simple	Toxic
Ethylbromacetate	Chloracetone
Xylyl Bromide	Bromacetone
Benzyl Bromide	Iodoacetone
Brommethylethyl Ketone	Acrolein
Ethyl Iodoacetate	Chlorpicrin
Benzyl Iodide	Phenyl Carbylamine Chloride
Brombenzyl Cyanide	
Chloracetophenone	

Toxic Lung Irritants which attacks the lungs like the simple lung injurants which follow, but also poison the body with arsenic. These include -

Phenyldichloroarsine
Ethyldichlorarsine
Phenyldibromarsine

Simple Lung Injurants which attack and injure the bronchial tubes and the lungs, are highly toxic, and often lethal. By injuring the tiny air sacs in the lungs, they cause fluid to pass from the circulatory system into the sacs and literally drown the victims in their own blood. These lung injurants are made mostly from chlorine or bromine and include -

- Chlorine
- Monochlormethylchloroformate
- Dimethyl Sulfate
- Phosgene
- Chlorpicrin
- Dichlordimethyl ether
- Methylsulfuryl chloride
- Ethylsulfuryl chloride
- Perchlormethylmercaptan
- Trichlormethylchloroformate
- Phenylcarbylamine chloride
- Dibromodimethyl ether

Vesicants are chemicals that vesicate (blister) the human or animal body surfaces on the outside or inside, wherever they come into contact with once living tissue. These include -

- Dichlorethyl Sulfide
- Chlorvinyldichlorarsine
- Dibromomethyl Sulfide
- Ethyl Dichlorarsine
- Methyldichlorarsine

Systemic Toxic Agents are those chemicals that penetrate the cell linings (lungs usually) without producing local injury and pass into the blood stream where they diffuse through the whole body systematically poisoning the tissues and in the end causes death by paralysis of the central nervous system. These include -

- Hydrocyanic Acid
- Cyanogen Chloride
- Cyanogen Bromide
- Phenylcarbylamine Chloride

Sternutators are respiratory irritants (sneeze producers) that are quick acting, non persistent in the envoirenment, and penetrate the gas masks used to stop all the other chemicals. These cause nausea, vomiting, and usually forced the soldier to remove their masks so the lethal chemicals could act on them. These include -

- Diphenylchlorarsine
- Ethyl Carbazol
- Diphenyl Cyanarsine
- Diphenylaminechlorarsine

The toxic lung injurants mentioned above all act as sternutators as well.

These chemical weapons behave differently than explosive and propelled weapons. While these weapons effect a target by direct physical impact or flying fragments, a chemical is transported to an area in a container and released where they mix into the surrounding atmosphere an saturate it where it may affect all individuals. The effect of projectiles and explosives in instantaneous and is over in a second, while chemicals may persist and injure or kill for hours or days. Chemicals can also filter into trenches and bunkers where defenders are sheltered from ordinary ordnance.

To understand what makes these chemicals effective in war and why they are selected and used over other chemicals, two more concepts must be understood- Toxicity and Persistence.

Toxicity in chemical agents varies greatly. We described in chapter two how to measure toxicity in animals and state it as an LD50 or LC50. Many of the acceptably deadly compounds tested before WW! were used in practice during the war with mixed results. We know that toxic chemicals react with living tissues on contact in different ways and destroy them by forming various deadly chemical combinations. The degree that the body becomes poisoned is proportional to the amount of tissue exposed and the ability of the chemical to cause lethal harm is therefore dependent on three variables.

1. The time of exposure to the toxic chemical.
2. The concentration of the exposure to the toxic chemical.
3. The concentration of the living tissues needed to be affected. (A larger person needs a bigger dose to produce the same level of poisoning equivalent to the greater weight or surface area of that person- the larger person usually eats more, breathes in more air with each breath, and presents more skin tissue so they usually get a proportionally larger dose.)

The fatal dose from normal inhalation of the WW1 poison gases for one minute is recorded and confirmed from war experience in the chart below. The amount is in milligrams per cubic meter of air. (One milligram is 1/454,000 of a pound or the 450 mg of phosgene is about 1/1,000 of a pound of agent in each cubic meter of air. This would be about one ounce distributed and mixed into the air of a 12'x12'x12' room and breathed for one minute to produce 100% fatalities.)

	1 hour	10 minute exposure LC50
Phosgene	450 mg	.5mg/liter
Diphosgene	500	.5
Lewisite	1,500	.12
Mustard Gas	1,500	.15
Chlorpicrin	2,000	2.00
Ethylsulfuryl chloride	2,000	1.00
Ethyldichlorarsine	3,000	.5
Ethylbromacetate	3,000	2.30
Phenylcarbylamine chloride	3,000	.5
Chloracetone	3,000	2.30
Benzyl Iodide	3,000	3.00
Methyldichlorarsine	3,000	.75
Acrolein	3,000	.35
Diphenylchlorarsine	4,000	1.50
Diphenylcyanarsine	4,000	1.00
Bromacetone	4,000	3.20
Chloracetophenone	4,000	.85
Benzyl bromide	6,000	4.5
Xylyl Bromide	6,000	5.6
Brombenzyl cyanide	7,500	.35
Chlorine	7,500	.2

Hydrocyanic acid can kill at 1,000-4,000 mg in one hour or .2 mg/liter in 10 minutes but its effects are chemically reversible. For comparison, the carbon monoxide used in assisted and unassisted suicides is toxic only at 70,000 mg dosage in one hour or at 5 mg/liter in 10 minutes.

Toxicity increases as exposure time increases and the effective dose can be decreased. The dose can also be increased and the time decreased to produce fatalities as the chart shows as well. Some chemicals are much more lethal at the higher doses than others as is shown in the chart. By increasing exposure time, the dose can be reduced to levels that are almost undetectable. The following chart shows the tiny doses required as phosgene is applied over 75 minutes to target animals.

Time of exposure	Minimum LD50 for Phosgene
2 minutes	2 mg/ liter
5 "	1.1
10	.65
15	.46
20	.37
25	.30
30	.27
45	.20
60	.17
75	.16

At 75 minutes the dose reduces very little (the point of diminishing returns).

Many of the chemical agents used were not intended to kill but to irritate to the point of incapacitating. There combat value would lay in their ability to produce intolerable effects on the enemy so that they could not fight back. If they did not have gas masks on and the attackers were protected with masks or protected clothing then it was very easy to overrun the enemy positions. If you think that the lethal doses for the chemicals were tiny, the doses needed to produce intolerable effects in one minute is very nearly chemically undetectable. The doses are measured in mg/liter for human tolerance for one minute.

Diphenylcyanarsine	.00025	Phenylcarbylamine chloride	.025
Diphenylaminechlorarsine	.0004	Brombenzyl cyanide	.03
Lewisite	.0008	Benzyl iodide	.03
Mustard Gas	.001	Ethylbromacetate	.04
Diphenylchlorarsine	.0012	Methylsulfuryl chloride	.04
Chloracetophenone	.0045	Dichlormethyl ether	.04
Bromacetone	.01	Diphosgene	.04
Ethyldichlorarsine	.01	Ethylsulfuryl chloride	.05
Ethyliodoacetate	.015	Chlorpicrin	.05
Xylyl bromide	.015	Acrolein	.05
Phosgene	.02	Dibromomethyl ether	.05
Methyldichlorarsine	.025	Benzyl bromide	.06

Cyanogen bromide	.06	Chlorine	.1
Cyanogen chloride	.061	Chloracetone	.1
Perchlormethylmercaptan	.07		

It is clear that the Diphenylcyanarsine is by far the most effective irritant and it produces strongly disagreeable symptoms at only .00000001 gram per liter of air.

Persistency in the envoirenment is an important element in choosing a chemical weapon. If the chemical is a pure gas, then it is distributed over the target area without any liquid or solid material being left on the ground. This means that it is only as persistent as the air. If the air is extremely still, then it may persist in an area until the normal mixing with air dilutes them out. The heavier than air gases will descend into trenches and depressions and this slows the dilution and adds to its persistence in these areas. The gas will follow the currents of air and are best used when it is released upwind of the target. These may be persistent in areas of dense vegetation.

Toxic smoke material sinks to the ground gradually according to the size of the particles and the ability of the wind to suspend them in air. Fine solid dust particles behave similarly.

Toxic liquids are dispersed by air exploding artillery shells and bombs which distribute the liquid in tiny droplets over large areas. The droplets fall on the targeted individuals as well as the ground and all other objects from which they slowly evaporate into the air. This provides a constant source of replacement of poison gas as the air carries away the evaporated material. As long as the liquid chemical persists on the ground, the air is constantly replenished with toxic gases.

All the chemicals turn to vapor at a rate dependent on the temperature. Mustard gas turns to a gas so slowly in cold weather that the liquid on the ground can barely produce enough gas to cause lung injuries. In hot weather, it always evaporates at a lethal rate, and yet economically enough that it would persist in dangerous amounts on the ground for up to three weeks (or longer if applied heavily). In comparison, phosgene evaporates so quickly in the summer that it is effectively gone in 15-30 minutes. This is due to the differences in vapor pressures of the chemicals. The higher the vapor pressure at a given temperature of air, the less persistent it is at that temperature (higher vapor pressure means it turns to a gas more quickly).

Some of the solid chemical agents first melt and then turn into the toxic gas. Mustard gas is a solid which melts at 13.9 C. Above this it becomes a volatile liquid. Phosgene boils at 8 C and rapidly evaporates away into a heavy gas. Although diphosgene begins to evaporate at this temperature, its persistence is 100 times greater than phosgene which means it evaporates much more slowly.

Many other factors affect the ability of these chemicals to injure or kill and these will be covered in later chapters. We will now describe how each of the chemicals are produced.

Lacrimators

Ethylbromacetate [CAS# 105-36-2 CH2BrCOOC2H5] was first used by the French in rifle grenade attacks in August 1914 and was not considered a poison gas which made it acceptable for the allies to use. By November, the French began to run out of bromine to make it and switched to producing chloracetone for its gas grenades.

It was first made in 1858 by chemists who mixed bromine, a highly reactive halogen, with acetic acid to produce Bromacetic acid. This was then mixed with ethyl alcohol and yielded the ethylbromacetate which immediately irritated the eyes of the chemists who discovered it. It was easy to make and handle and was used in 1912 by the Paris police in temporarily disabling and arresting criminals and gangs.

Modern production is accomplished by mixing bromine with acetic acid in the presence of red phosphorus (to speed up the reaction) and then adding the ethyl alcohol or its alkane equivalent ethylene. Dry bromine is extracted from natural brines and seawater by oxidation of bromine salts with chlorine. It is sold in both liquid and dry forms. acetic acid is sold in dry concentrated forms or as dilute liquid (vinegar). Ethyl alcohol is widely available as a gas substitute. This liquid is transparent with a specific gravity of 1.5 and it boils without decomposition at 168 C (334.4 F). It is slowly broken down by water and is insoluble in it. It irritates the eyes and nasal passages at .003 mg/ liter and causes lacrimation at .04 mg/ liter where it is intolerable to the eyes. It is lethal at 10 minutes exposure at 2.3 mg/ liter making it twice as toxic as chlorine gas. Its volatility is 21 mg/ liter at 68 F so it can easily reach 10 times its lethal dose on a comfortable day.

Chloracetone [CH3COCH2Cl] also known by the French as "Tonite", was substituted for Ethylbromacetate in 1914 when the Bromine ran out. It was easily made directly mixing chlorine into acetone to produce a clear liquid that boils at 119 C (246.2 F) with a specific gravity of 1.16. The vapors are slowly produced that are 3.7 times heavier than air. It is only slightly soluble in water and is not broken down by it, but the liquid slowly polymerizes on storage and has a shelf life of only a few months.

It has a pungent odor like hydrochloric acid and lacrimates the conjunctiva (eyes) at .018 mg/ liter and reaches intolerable levels at .1 mg/ liter in one minute. It is lethal in 10 minutes at a concentration of 2.3 mg/ liter making it almost as toxic as the ethylbromacetate above but because it can reach much higher concentrations in air and is much more volatile, it is more effective and faster at killing the targets.

The first gas masks used charcoal which readily absorbs chloracetone so the hunt began for better tear gas that an enemy could not stop with the charcoal based gas masks and by 1915, the French had developed bromacetone with other newer and better lacrimators on the way.

Xylyl Bromide [CAS# 28258-59-5 $C_6H_4CH_3CH_2BR$] also known as *a*-bromoxylene or T-Stoff, it was developed by the Germans early in the war as they realized that most lacrimators were more effective using bromine instead of chlorine in the corresponding compounds. The German chemical industries were well developed for production of Bromine so there was no shortage of this raw material as there was in France and Britain. On January 31, 1915, it became the first gas in the history of war to be fired in an artillery shell on the Russian front at Bolimow.

Xylyl Bromide is made by first obtaining Xylene from coal tar or petroleum distillation (already described in Vol's 3 and 4) and directly Brominating it (mixing it with Bromine). When pure it is a light yellow slightly viscous liquid with some solids in the crude form which turns it to a black liquid. It has a specific gravity of 1.4 and boils at 410-428 F (210-220 C) producing a pungent aromatic vapor which smells like lilacs and is 8.5 times as heavy as air. It corrodes iron and steel rapidly and must be stored in lead or plastic lined containers. It is also combustible and can ignite in air.

Xylyl Bromide irritates the conjunctiva in concentrations as low as .00027 mg/ liter and affects the lacrimal glands at .0018 mg/ liter. At .015 mg/ liter it becomes intolerable in about one minute and at the 5.6 mg level is lethal in about 10 minutes. This makes it a less toxic but more powerful lacrimator than ethylbromacetate. This liquid has a low volatility (.6 mg/ liter at 68 F) and so is not very effective in cold weather and is easily absorbed by charcoal in gas masks. These physical characteristics soon caused a search for a replacement. It is used in modern tear gas formulations.

Benzyl Bromide [$C_6H_5CH_2Br$] chemical name *a*-bromotoluene was developed by the Germans as a more volatile replacement for xylyl bromide. It still has a low volatility of 2.4 mg/liter at 68 F, low vapor pressure of 2mm of mercury at 20 C, and great chemical stability which made it very persistent everywhere it was used. It was less irritating than xylyl bromide however requiring a concentration of .004 mg/ liter to irritate and .06 mg/ liter to become intolerable. As its concentration increases it irritates the nose, throat and bronchial tubes producing salivation and nausea, until at 4.5 mg for 10 minutes it finally kills.

The Germans called the material T-Stoff while the French produced version was called "Cyclite". Like the other bromide compounds, it corrodes steel and iron and must be kept and delivered in lead, enamel, or plastic lined containers. It also is corrosive to skin in high concentrations.

Charcoal completely absorbs its vapors. This combined with its low irritation level caused it to fall into disfavor as a tear gas quickly.

It is made by directly brominating toluene as in WW!, or by reacting hydrobromic acid with benzyl alcohol as is done in modern processes. It is used today to make foaming and frothing agents in industry and in organic synthesis. The use of toluene for explosives in WW1 made for a shortage of raw materials for this compound during the war.

Bromoacetone [CH_3COCH_2Br], called B-Stof by the Germans, Martonite by the French, and BA by the United States, was quickly developed by the Germans in their efforts to find a more easily volatilized irritant. It rapidly became the most popular pure lacrimator with over 1,000 tons used in artillery projectiles alone. Bromacetone is the bromine equivalent to chloracetone and is made the same way, by brominating acetone directly. It is a colorless liquid that boils at 135 C with a vapor 4.7 times heavier than air. In storage, bromacetone slowly decomposes into a black resinous mass which gradually evolves hydrobromic acid. This decomposition is accelerated by exposure to heat and light, although it is not affected by water.

Bromacetone is one of the most effective lacrimators ever used in war. It irritates the eyes at .0015 mg/ liter and is intolerable at .01 mg. At 3.2 mg, it is fatal in a ten minute exposure making it in-between in lethality.

At 20 C (68 F), the vapor pressure of bromacetone is 9 mm of mercury, its volatility is 75 mg per liter and its specific gravity is 1.6. Because of its higher volatility, bromacetone quickly reaches toxic levels once dispersed in the field. This makes it a toxic lacrimator as well and its liquid droplets also produce blisters on contact with skin and are very painful. The wounds heal quickly once the exposure is removed.

Both sides used bromacetone in artillery and mortars, but demand for acetone for other war supplies led the British to explore the related iodine compounds as lacrimators.

Brommethylethyl Ketone [$CH_3CO.CH.Br.CH_3$] known as Bn-Stoff by the Germans and Homomartonite by the French, evolved as a result of shortages of acetone. Demand for acetone as a solvent to make nitrocellulose for gun propellants became crushing and effectively brought production of bromacetone to a standstill on both sides.

A material called methylethyl ketone is produced as a byproduct in acetone oils when acetone is manufactured from wood. By brominating this material like the acetone, brommethylethyl ketone is produced containing both methyl and ethyl alcohols. When first distilled, it is faint yellow liquid that is insoluble in water and boils with decomposition at 293 F (145 C) with a vapor that is 5.2 times heavier than air. It has a specific gravity of 1.43 and a vapor pressure of 15 mm at 14 C (57.2 F) with a volatility of 34 mg/ liter at 20 c (68 F). It is more volatile and therefore less persistent than xylyl bromide.

Like the other bromine compounds, bromine resistant plastics, lead, or enamel coated metals must be used to prevent corrosion and permit storage.

Brommethylethyl ketone produces lacrimatory symptoms at .0126 mg /liter, is intolerable at .016 mg/ liter, and is toxic in 10 minutes at 2 mg/ liter. Because it has both high toxicity and high volatility, it can be used a lethal agent as well as a lacrimator. Overall it was considered less effective than bromacetone, but was the only option when faced with raw material shortages and was developed solely for economic reasons.

Iodoacetone [CH3COCH2I], called Bretonite by the French, was developed by the French and British as an alternative to the bromine based gases because of the short supplies of bromine. The three iodine based compounds we will now describe were quickly produced to provide a reliable source of gas weapons. All three were more toxic and irritant, but less stable than the corresponding bromine compounds.

The French first used Iodoacetone as an artillery shell filling in August 1915, but it was soon replaced by Benzyl Iodide, while the British soon replaced their stocks with Ethyliodoacetate.

Iodoacetone is made by mixing a solution of alcohol with chloracetone dissolved in it, with either sodium iodide or potassium iodide. The chloracetone is converted to iodoacetone with an alcoholic chlorine solution left over. It is a faint yellow liquid that turns brown in contact with air and has a specific gravity of 1.8. It boils at 102 C (215.6 F) and decomposes on heating. It converts to diiodoacetone on standing for about one week.

It is the most toxic halogenated ketone, while producing lacrimation at .0126 mg/ liter and has a very pungent odor.

Ethyliodoacetate [CH2ICOOC2H5] also called SK by the British, it is a dense colorless oily liquid that is decomposed by light, air, and alkaline solutions with water in which it produces liberates iodine. It has a specific gravity of 1.8, boils at 179 C (356 F), a vapor density of 7.4 at .54 mm at 20 C.

It is produced by mixing ethyl acetate, bromoacetate, or chloracetate with potassium iodide. It is also made by the decomposition of ethylchloracetone in an alcoholic solution with potassium iodide or sodium iodide added. It does not corrode metals and can be loaded into regular shells and storage containers.

It yields 3.1 mg/ liter at 68 F making it a persistent and powerful lacrimator. It irritates at .0014 mg/ liter, is intolerable at .015 mg/ liter, and becomes lethal at 1.5 mg/ liter in 10 minutes.

By the time of its first use by the British on Sept 24, 1915, it was the most powerful and toxic of all the lacrimators. Its toxicity was 1/3 that of phosgene, but its volatility was so low that it did not produce deaths on the battlefield. To make it more volatile, it was mixed with alcohol and loaded into shells. The British used it in large quantities because of the shortage of bromine and the large supplies of iodine they could import from South America.

Iodine is too expensive today to consider for use in tear gas agents. There are other less expensive and more effective compounds available today.

Benzyl Iodide [C6H5CH2I] was called "Fraissite" by the French and was first used by them in November 1915. It replaced iodoacetone because of the acetone shortage and was used in the same manner as the benzyl bromide of the Germans.

Benzyl iodide was produced by dissolving benzyl chloride in alcohol and then treating it with potassium or sodium iodide. It is manufactured commercially today by reacting benzyl chloride directly with hydroiodic acid.

It is a white crystalline solid that melts at 24 C (75 F) and boils with complete decomposition at 226 C (438 F). Its specific gravity is 1.7335, it is insoluble in water, soluble in ether, carbon disulfide, and alcohol. It undergoes double decomposition in storage and is best prepared as a binary weapon in the iodic acid and benzyl chloride form.

Benzyl Iodide is about twice as powerful at irritation as benzyl bromide at .002 mg/ liter, is intolerable at .03 mg/ liter, and is fatal at 3 mg/ liter for 10 minutes. Its volatility is only 1/2 that of benzyl bromide and was mixed 50/50 with benzyl chloride by the French to increase its concentration in air. The French only used it for a short time and soon replaced it with Acrolein and other newly developed lacrimators.

Acrolein [CAS# 107-02-8 CH2CHCHO] was also called "Papite" by the French. It was used as a substitute lacrimator during the bromine and acetone shortages. During WW1 it was manufactured by heating and dehydrating glycerin and distilling it while using potassium bisulfate or crystallized magnesium sulfate catalyst. Modern production involves oxidation of either propylene or allyl alcohol, heating glycerol with magnesium sulfate, or heating propylene in the presence of a bismuth-phosphorus-molybdenum catalyst.

It is a clear or yellowish liquid with a pungent choking odor. It is soluble in water, ether, and alcohol. It has a specific gravity of .84 at 15 C and boils at 52 C (125.6 F) yielding a light vapor that is 1.9 times as heavy as air. It is a very reactive gas that easily ignites in air.

During WW1, it was unstable and would rapidly oxidize to acrylic acid. When stored in inert gas it would polymerize gradually into acrolein gum which was no longer effective as a lacrimator. The storage problems were solved in modern practice by adding hydroquinone at 1-5% which inhibits the reactions effectively. During WW1, the French attempted to stabilize it with 5% amyl nitrate which was effective only on the polymerization.

Acrolein is a powerful lacrimator attacking both the eyes and the throat simultaneously, which makes it a lung injurant toxic gas as well. At only .007 mg/ liter, it irritates the conjunctiva as well as the mucous membranes of the respiratory tract. At .05 mg/ liter it is intolerable, and at .35 mg/ liter it is lethal in 10 minutes.

Acrolein was considered a failure during WW1 because of its lack of stability. Modern processes have solved this problem and it can be considered a potential war candidate today. It is used in herbicides, as a warning gas, and widely used as a chemical intermediate..

Chlorpicrin [CCl3NO2] is a strong lacrimator producing symptoms as low as .002 mg/ liter. At .05 mg/ liter it is intolerable and at 2 mg/ liter it is fatal in 10 minutes exposure. Chlorpicrin is also classified as a lung injurant toxic gas where it is much more effective but we will cover its physical and chemical properties here.

Chlorpicrin was called "Vomiting gas" by the British, "Aquanite" by the French, and "Klop" by the Germans. The United States used the designation PS for the material. It was first used by the Russians in August 1916 and quickly adopted by the other nations for use in mortars and artillery shells, as well as gas cylinders for gas cloud attacks. It was possibly the most widely used gas in the war.

Chlorpicrin was discovered by an English chemist in 1848 and was well known at the start of WW1. It is a colorless oily liquid that boils at 112 C (231.5 F) and is 5.6 times as heavy as air. It has a specific gravity of 1.66 and produces a sweet odor similar to flypaper. It evaporates very quickly and in concentrations, its vapors become pungent and irritating. Its vapor pressure is 18.3 mm at 68 F and its volatility is 165 mg/ liter. It was often mixed with 70% chlorine for cloud gas attacks and this mixture was called Yellow Star gas by the British.

Chlorpicrin is very stable. It does not react with water, acids, or alkalis or any of the chemicals in the gas mask canisters used in WW1 except charcoal which offer only limited protection and was quickly used up. It is easily manufactured by directly mixing chlorine bleach with picric acid (chlorinating it). In mass production, ordinary bleaching powder is dissolved in water and heated with live steam. In Volume 3 we taught how to make Picric Acid from aspirin for explosives so we will not repeat it here. Because it was widely available with bleach powder it was easy to produce in volume by all the countries. The picric acid was mixed with lime water and then mixed into the reactor with the steam heat. The chlorpicrin was distilled off with water vapor and separated from the water (it is insoluble in water).

Because it is a lacrimator and it could also penetrate gas masks that protected against chlorine and phosgene, it was often employed in combination with the acid gases. Chlorpicrin also injures the stomach and intestines in tiny amounts resulting in nausea, vomiting, colic, and diarrhea. These conditions would persist for weeks and produced very high casualty rates in the field by itself. When combined with the other gases, the chlorpicrin would irritate enough to force many soldiers to remove their gas masks exposing them to other lethal agents like phosgene.

Chlorpicrin had the disadvantage of decomposing from the heat and shock of the bursting charges of the mortars and artillery shells and the casings had to be made thinner walled to accommodate smaller charges. Chlorpicrin did have the advantage of a persistency of 3 hours or more on the ground. It was two and a half times as lethal as chlorine gas but only one fourth as lethal as phosgene, It was an effective war gas but was soon replaced by more deadly and effective poison gases of the war.

Phenylcarbylamine Chloride [CAS# 622-44-6 C6H5NCCl2] also known chemically as Phenylisocyanide Chloride, it was called "Green Cross" by the Germans and it acts as both a lacrimator and a toxic lung injurant. It produces lacrimation at .003 mg/ liter, is intolerable at .025 mg in one minute, and is toxic in 10 minutes at .05 mg/ liter. It was used briefly by the Germans in May 1917 as the last of the simple lung injurants and was replaced in two months by the new vessicants (mustard gas was the prototype) and the sternutators (Diphenylchlorarsine).

This gas was produced in an attempt to make a more persistent material that would exhaust the gas mask canisters and then cause subsequent lung injury. It was later used with mustard gas to mask its odor.

The Green Cross was made by first mixing carbon disulfide or thiophosgene into aniline with a reaction taking several hours. This yielded a material called mustard oil (C6H5NCS) also known as phenylisothiocyanate . This was then directly chlorinated to produce the phenylcarbylamine chloride. The mustard oil can also be made by reacting hydrochloric acid with sulfocarbanilide. It is also toxic with lacrimatory properties.

It is a transparent liquid with a specific gravity of 1.3 at 15 C, boils at 208-210 F (105 C), and produces a vapor 6 times heavier than air. Its volatility is 2.1 mg/ liter at 68 F (20 C). It has an onion like odor that is soluble in alcohol, benzene, and ether and is insoluble in water.

Phenylcarbylamine chloride lacrimates at 1 ppm or at .0072 mg/ liter and irritates at about 1/2 this level. It is intolerable at .025 mg/ liter and is fatal in 10 minutes at .5 mg/ liter. It was mainly used in 105 and 150 mm artillery shells and was very persistent where it was used making it impossible to use on the tactical offensive. The low vapor pressure often prevented effective concentrations in winter. About 700 tons were used in the war without producing high levels of casualties.

Brombenzyl Cyanide [C6H5CHBrCN] was the last and the most effective lacrimator used in the war. It was called Camite by the French and "CA" by the Americans and used by both countries in 1918.

It was discovered in 1881 by brominating phenyl cyanide and was produced commercially in private industry in 1914. It is made industrially by

1. Chlorinating toluene to produce benzyl chloride.
2. Dissolving sodium cyanide in alcohol and adding the benzyl chloride to form benzyl cyanide.
3. Adding Bromine vapor in the presence of sunlight to the benzyl cyanide

Brombenzyl Cyanide is a yellow white crystalline solid that melts at 77 F (25 C) into a brown oily liquid with a specific gravity of 1.47. It boils at 437 F (225 C) and decomposes slightly in air after which it is very stable. It decomposes very rapidly when heated above 302 F (150 C). It is soluble in water which decomposes it very slowly and is soluble in phosgene, chlorpicrin, and benzyl cyanide. Its vapor pressure is .012 mm of mercury at 20 C (68 F), and its volatility is .13 mg/ liter at the same temperature. It is so persistent that it lasts for 3 days in open country and seven days in the woods. If mixed into the ground, it maintains vapors for 15-30 days.

Like the other bromine compounds, it must be stored in plastic, glass, porcelain, enamel, or lead lined containers because it corrodes most metals.

It has a sour fruit odor and produces a burning sensation in the mucous membranes. When it lacrimates the eyes, it also generates headaches. It irritates at .000087 mg/ liter which is the same as one part in one hundred million (1-100,000,000). It lacrimates at .0003, is intolerable at .0008, and is lethal at .9 mg/ liter in 30 minutes. Because of its low toxicity and volatility, it is hard to produce toxic concentrations in the field.

Its drawbacks are the need for special linings for the containers, it slowly decomposes in storage, and the heat of the bursting charges in the artillery shells decomposes it making it hard to deliver by projectile. Its persistency in soil can be a drawback to the side that is on the offensive.

Chloracetophenone [$C_6H_5COCH_2Cl$] was developed by the Americans as "CN" agent. It was discovered by a German chemist in 1869 who described its effects on the eyes. It was difficult to manufacture and no CN was actually used in the war.

After the war, American scientists worked out the problems in mass producing it for use in war. The steps they developed to manufacture it are -

1. Chlorinating acetic acid directly to produce monochloracetic acid

$$CH_2COOH + Cl_2 = CH_2ClCOOH + HCl$$ (hydrochloric acid)

2. This was then chlorinated with both chlorine and sulfur monochloride to produce Chloracetyl chloride

$$3Cl_2 + S_2Cl_2 + 4CH_2ClCOOH = \$ \ CH_2ClCOCl + 2SO_2 + 4\ HCl$$

3. The chloracetyl is then treated with benzene in the presence of anhydrous aluminum chloride which acts as a catalyst.

$$CH_2ClCOCl + C_6H_6 = C_6H_5COCH_2Cl + HCl$$

This material is a solid that does not corrode metals and is resistant to heat and moisture. It does not corrode metals and is not decomposed by water.

Its crystals are colorless producing a vapor that smells like apple blossom. It has a specific gravity of 1.3, melts at 59 C (138 F), and boils at 247 C (476 F) producing low vapor concentrations in air. Its vapor pressure is .013 mm and its volatility is .106 mg/ liter. Because it is not decomposed by boiling, it can be distilled and poured into weapons canisters or shells while molten. Explosives do not affect it and it can be mixed right in with the bursting charges which can also be high explosives.

It lacrimates at .0003 mg/ liter and is intolerable at .0045 mg/ liter. It is toxic at .85 mg/ liter at 10 minutes. It also irritates the upper respiratory tract and irritates the skin as well producing itching and burning sensations on moist skin surfaces similar to sunburn. The symptoms go away in a few hours.

A mixture of 3/4 black powder and 1/4 CN can burn progressively without explosion which effectively disperses the material in grenades, mortars, artillery shells, and bombs. It is also soluble is solvents which led to its being used in liquid formulations as follows.

1 CNB made up of CN, Benzol, and Carbon Tetrachloride

2. CND made of CN, and ethylene dichloride

3. CNS made up of CN, Chloroform, and Chlorpicrin.

In high concentrations at low temperature, it exists as smoke particles rather than vapor and the tiny particles do not react with charcoal in gas mask canisters which means that a mechanical particle filter or trap is necessary in the mask to protect against it.

This material has been widely used as the training gas in the military boot camps, and for suppressing internal disorders and mobs.

Nitrogen and other Mustards

Mustard agent developed during WW1 consisted of di-chloroethyl sulfide that is a colorless oily liquid with a garlic or horse radish like odor. It was used mainly as a Vessicant which caused blisters over the entire body and through most ordinary clothing so that the entire body had to be protected with special materials. It would attack the eyes and lungs and acted as a systemic poison as well. The gas was colorless and the targets were generally unaware they were even attacked because the damage and injuries did not appear for several hours. The bromine analog was also used during the war in which bromine replaced the chlorine in its process and manufacture.

After WW1 and during WW2, many sulfur analogs to mustard gas were investigated and a large number of potent vessicants were discovered. The ones developed and used by the United States were -

1,2-bis (2-chloroethylthio) ethane, also called chemical agent "Q" for
$ClCH_2\ CH_2\ SCH_2\ CH_2\ SCH_2\ CH_2Cl$

bis (2-chloroethylthioethyl) ether, also called chemical agent "T" for
$ClCH_2\ CH_2\ SCH_2\ CH_2\ OCH_2\ CH_2\ SCH_2\ CH_2Cl$

These differed from the original mustard agent in that each chloroethyl group has its own sulfur atom associated with it instead of sharing it in the original formula. Both of these are more Vessicant than mustard and neither is as volatile which makes them less effective by the vapor route.

The US manufactures the original mustard and modifies it during manufacture to yield the above formulas in a mixture. The end process yields a mix of HQ (Mustard is H), or HT. The reasons for making these mixtures is that the sulfur mustard melts at 10 C and would solidify in airplane spray tanks, spray bombs, and spray based artillery shells. In a mix, the melting point is raised, both are more toxic, more Vessicant, and more persistent than when the mustard is used alone. This makes the combination weapons more effective.

In wartime, mustard gas is distributed primarily to restrict the use of terrain or mobility of an enemy. An area is saturated with mustard and within a few hours the enemy soldiers begin to experience blisters that do not heal and become infected easily. Over time, the body becomes more sensitive to the mustard agents so that doses are more than cumulative. They were used against Abyssinia and by the Japanese in China during WW2, and were used by the Iraqi's against Iran in the 1980's killing 500-1,000 soldiers and injuring 40-50,000 more. US field commanders had stockpiles of mustard and other poison chemical agents that they were authorized to use during the later phases of the war against Japan in WW2. Mustard also caused injuries during WW2 when the Germans bombed a cargo ship in the Italian port of Bali. The ship was loaded with canister's of mustard agent and they leaked out and mixed with the sea water causing a number of injuries to local civilians and US sailors.

Fisherman and sailors off of Denmark and Sweden have also been injured from mustard gas brought up in cylinders entangled in their fishing nets. Almost all the poison gas storage containers for all nations were dumped into the oceans after WW2. This practice has been suspended by most nations today.

The Aum Shinri Kyo sect had produced several hundred pounds of mustard agent for use as a weapon in 1995 in Japan (as well as the nerve agent they used in the subways) but the alleged stocks were destroyed before police raided the cults laboratories.

Other improvements on the original mustard agents include mixing it into and absorbing onto diatomaceous earth (called dusty or micronized mustard) which makes it easier to disperse from bomb and missile warheads. It is also mixed with Lewisite to lower its freezing point to -26C. It can be mixed with polymers to thicken it and decrease its volatility which increases its persistence.

Mustard can also be distilled (called HD) and purified by chemical washing and vacuum distillation. This gets rid of the mustard odor making it nearly impossible to detect without special equipment and adds to its storage stability. The end product is usually 2,2-dichloro-diethyl sulfide.

A detection reagent called *p*-nitrobenzylpyridine has been developed which allows for the detection and estimation of dosages in the air for most of the mustards. When the chemical is treated with alkali, it will detect concentrations of mustard as low as .1 mcg or about 1 part per million in air.

Nitrogen Mustards were first synthesized by scientists in 1935 and produced marked Vessicant actions on living tissue. Published reports in both the US prior to WW2 show that both the US and German scientists were well aware of their properties and potential uses in war. Germany began production of Nitrogen mustard in 1941, the Americans began production in 1943, and the British never began actual production following an explosion at their only planned facility during the war.

Nitrogen mustards are easily made by first taking ammonia and replacing its hydrogen atoms with different organic materials. This new molecule is then reacted with the chloroethyl groups in place of the sulfur used in the sulfur mustards. The nitrogen mustards are more Vessicant, toxic in other ways, and generally odorless, all of which makes them a better choice for use as a weapon of war. Since ammonia is the primary source of the key reaction molecule, it is less costly, produced from the air, and generally more available than sulfur for which supply may be restricted in wartime or where the sulfur is needed for explosives.

The nitrogen mustards used by the US are -

HN-1 1,2,2 dichloro-triethylamine
HN-2 N-Methyl-2,2-dichlorodiethylamine
HN-3 tris(2-chloroethyl)amine

The HN-2 formula is considered too unstable for storage and use by most nations. All the nitrogen mustards are generally odorless although some can be detected as having a fishy or soapy smell when large amounts are present but these odors are easily masked. [The reason these odors are known is due to the large number of injuries reported in German chemical factories that were making it after WW2. This was possibly due to the need to supply the heavily outnumbered US forces in Germany as well as new commercial uses as side chains for synthetic drugs.]

Nitrogen Mustards can be made in a variety of ways and we will start with the basic building blocks here. First, ammonia or urea (NH2-CO-NH2) is reacted with an alcohol or alkane to yield and amino alcohol.

The starting building material is usually an amino ethanol. The word amino simply means a molecule built around Nitrogen (N), and ethanol is the alcohol you are already familiar with.

An **amino ethanol** usually has a formula of

where R can be any alcohol or other element

```
R
  \
   N - CH2 CH2 OH
  /
R
```

Ethylene Imine is also a simple building block

It is made by reacting ethylene dichloride
with ammonia using an acid receptor

```
CH2
   \
    N - H
   /
CH2
```

Ethyl Amine is made by reacting ethyl chloride
with alcoholic ammonia under heat and pressure

```
H
  \
   N - CH3 CH2
  /
H
```

Ethanolamine (MEA) is made by reacting
ethylene oxide and ammonia to give a mix of
Mono, Di, and Tri, Ethanolamines
The mono form is at the right

```
H
  \
   N - CH2 CH2 OH
  /
H
```

When an Amino Ethanol is reacted with Thionyl Chloride, a chemical reaction takes place as follows -

```
R
  \
   N - CH2CH2 OH        plus     SO Cl2 (Thionyl Chloride)
  /
R
```

The result is

```
R
  \
   N - CH2 CH2 Cl-HCl   plus SO2 gas
  /
R
```

This can form a substance called

DEA Diethyl-*B*-chloroethylamine

```
CH2 CH3
        \
         N  -  CH2 CH2 Cl-HCl
        /
CH2 CH3
```

or another substance called

DMA Dimethyl-*B*-chloroethylamine

```
CH3
    \
     N  -  CH2 CH2 Cl-HCl
    /
CH3
```

The only difference in the above formulas is the use of ethanol versus methanol as the alcohol source in its manufacture (Ethanol = CH2 CH3 while Methanol = CH3)

These salts created above are solids of low vapor pressure, are insoluble in fat solvents, and are generally non-toxic. These are the hydrochloric salt forms of the amines. When caustic soda is added, the chlorine is removed by reaction and the molecule becomes very toxic and produces symptoms resembling the full nitrogen mustards. Accidents in commercial production have resulted in serious injuries from the above reactions. The idea of using caustic to drive off the chlorine in water is also a good binary weapon idea since the salt is relatively safe to handle until the reaction takes place.

The true nitrogen mustards have at least two chlorine molecules plus the carbon linked to the nitrogen which form what is called a "labile ring" as diagrammed. The chlorine is liberated when the material becomes dissolved in water and a carbon chain is formed. The water can be that found in human tissues, blood, and inside of cells.

```
R    CH2
 \  /
  N  |       plus Cl-
 /  \
R    CH2
```

The liberation of two molecules of chlorine instead of one causes the mustard to be much more reactive and toxic.

HN1

```
CH2 CH3
      \
       N - CH2 CH2 Cl
      /
CH2 CH2 Cl
```

HN2

```
CH3
      \
       N - CH2 CH2 Cl
      /
CH2 CH2 Cl
```

HN3

```
CH2 CH2 Cl
      \
       N - CH2CH2Cl
      /
CH2 CH2 Cl
```

HN3 contains the most chlorine groups and is considered the most reactive and most toxic.

The toxicity of the mustard and related compounds are listed below in LD50 in mg/kg

	Mouse-LD50
HN1	1.2-13
HN2	2-29
HN3	2-7
Isopropyl bis *(B*-chloroethyl) amine	1.1-22

Nitrogen Mustard Derivatives	
Ethyl-B-Chloroethyl-ethylenimonium picrylsulfonate	2.0
Ethyl-B-Chloroethyl-B-hydroxyethyl picrylsulfonate	8.0
Ethyl-B-Hydroxyethyl-ethylenimonium picrylsulfonate	5-5.5
Methyl-B-Chloroethyl-ethylenimonium picrylsulfonate	2.4
Methyl-B-Chloroethyl-B-hydroxyethylamine hydrochloride	16-34
Methyl-B-acetoxy-ethylB-chloromethyl-amine	36
Methyl-B-hydroxy-ethyl-ethylenimonium picrylsulfonate	3.2-7.5
The Bunte salt of HN2	200-500
N,N'-dimethyl-N,N'-bis (B-dichloroethyl)-piperazinium dichloride	500

The Bunte salt above is produced by reacting inorganic thiosulfates with the mustard. They alkylate phosphates in a similar manner and this reaction can be used to detoxify the mustards somewhat.

Compounds related to Nitrogen Mustards	LD50 Mouse
Methyl-B-Chloro-ethylamine	100
Ethyl-B-chloro-ethylamine	100
Diethyl-B-chloro-ethylamine	100
Bis (B-chloroethyl)-amine	20-33
Allyl-bis (B-chloro-ethyl) amine	4-6
Vinyl-B-bis (B-chloro-ethyl) amino-ethyl sulfone	2.55
N,N,N'N'-tetrakis-(B-chloroethyl)- ethylenediamine dihydrochloride	7.5-26
Dimethyl-bis(B-chloroethyl) ammonium chloride	100-200
Bis(B-chloroethyl)-morpholinium chloride	100
Bis(B-chloroethyl)-chloramine	50
Bis(B-chloroethyl)-nitrosoamine	100-200
Bis(B-chloromethyl)-formamide	300-500

Other forms of Mustard include amino glucose mustards in which sugars are included in the amine attached to the Nitrogen as well as other forms. Examples include -

1,6-di(2-chloroethyl)amino-1,6dideoxy-D-mannitol
5-[Bis(2-chloroethyl)amino]-2,4(1H,3H)-pyrimidinedione   C8H11 Cl2 N3 O2
N,N-Bis(2-chloroethyl)aniline   Ph N (CH2 CH2 Cl)2

Triethylene Melamine (also known as TEM-CAS#51-18-2)
NC [N(CH2)2] NC [N(CH2)2] NC [N(CH2)2]

Triethylenephosphoramide (also known as APO-CAS# 545-55-1C010)
(NC2 CH2)3 PO

All the above are also highly toxic and represent only a small fraction of the possible permutations of mustard that are known or are yet to be discovered.

Non Phosphorus Toxic Military Chemicals Since WW1

More than 25 million new chemicals have been reported in the Chemical abstracts as of 1997 with most of these being toxic to one degree or another to humans. Some of these have properties that make them suitable for candidate consideration as military weapons, and, as they are reported, these are evaluated by the military scientists of the major nations for their possible use as war material.

Most of the chemicals used by the military are liquids that can be stored indefinitely in cylinders for rapid deployment. Some of these are stored under pressure in these cylinders so that they boil off as a gas once the tank or vessel is ruptured. Almost all volatalize into a gas form once they are released. The faster the gas volatilizes into the atmosphere, the higher the concentration in the air and the more toxic it is. The slower it is released, the lower the dose but the more persistent it is. This is especially true of chemicals that do not easily hydrolyzed (break down) in the envoirenment.

The chemical agents are usually stored in these vessels and are then distributed either mechanically or by bursting explosives and disseminate in the air as aerosol droplets or fine dust clouds. Some are mixed with solvents like DMSO which help carry them through the skin. Most of the chemical weapons of choice today are also odorless and colorless so that an enemy does not know they are being gassed and cannot easily identify them even if they see a cloud form from incoming ordnance.

The following chemicals have been mass produced for use in war by the major nation since the end of WW1 because they mostly fit the above physical requirements and will be described in alphabetical order here.

Allyl Alcohol

is also known as 2-propene-1-ol and as propenyl alcohol. CAS# 107-18-6, its formula is H2C=CHCH2OH. It is a colorless liquid with a pungent, mustard like odor. It boils at 96.9 C, melts at -129 C and has a bulk density of 7.11# per gallon. It is miscible with alcohol, water, chloroform, and ether. It was known to be a toxic alcohol by itself like all the other alcohols and it was known in the early 1920's that it was more than 100 times as toxic as ethanol and methanol and it is easily absorbed through the skin.

Allyl alcohol is used in the manufacture of many organic poisons (herbicides) including the nerve agents covered in the next chapter. It was first prepared in 1921 by reacting C3H5(OH2)2 with Oxalic acid (or in a separate procedure using formic acid) under heat and vacuum. [J. Chem. Soc. #119, 1301-6 (1921) and Organic Synthesis I 15-9 (1921).] It is produced in volume in modern industry by making allyl chloride from propylene and hydrolyzing it with dilute caustic soda, or isomerizing propylene oxide over a lithium phosphate catalyst at 230-270 C, or by simply dehydrating propylene glycol. It is used industrially to make resins and plasticizers, glycerol, acrolein, and many other pharmaceuticals and organic chemicals.

Arsine

also known as arsenic hydride or trihydride (AsH3), CAS# 7784-42-1 and designated SA by the US military, it is a colorless gas that boils at -62 C and decomposes at 230 C. It is soluble in water and slightly soluble in alcohols and alkali. It is highly toxic by inhalation and is used commercially in organic synthesis and as a doping agent for solid state electronic components as well as military poisons. It is easily made by adding water or hydrochloric acid to aluminum arsenide powder in which the gas immediately comes off in volume making it a portable solid weapon that is easily converted to gas in the field. It can also be easily made by adding most arsenic compounds to electrochemical cells in acid solutions. The arsenic quickly forms with the free hydrogen once the electricity is turned on and the Arsine evolves from the solution as a gas and can be recovered and compressed.

Other forms of field improvised manufacture include reacting zinc powder with hydrochloric acid and arsenic trioxide to yield the hydrogen gas in solution which then reacts with the arsenic to form the arsine which comes off as a gas. Dilute sulfuric acid (battery acid) has also been mixed with zinc arsenide to yield the gas in field conditions.

The gas is heavier than air and is useful in saturating targeted and enclosed areas

Arsine is a deadly toxic form of arsenic that has an LD50 of
1 part in 100,000 in 3 hours
1 part in 60,000 in 1 hour
1 part in 4,000 in 1/2 hour
1 part in 2,000 in 5 minutes

Arsenic poisoning is something that is often not tested for in most civilian deaths and this has made it a favorite assassins weapon. At low levels it is odorless and colorless and at lethal concentrations produces a garlic odor. It is considered a blood poison and causes long term injury to the kidneys and liver at low doses. Slight exposure causes headaches followed by chills, nausea, and vomiting yielding a vomit agent effect at larger doses. Anemia usually follows exposure.

At sublethal doses, the targets experience anorexia and a weak pulse. Most people exposed to sublethal doses in industry generally recover in 3-4 weeks with most of the arsenic being excreted in the urine. Industrial injuries were reported early this century in workers exposed to small amounts of arsine from the zinc arsenide and hydrochloric acid reactions described above.

Bromophosgene

also known as carbonyl bromide and carbon oxybromide is a heavy colorless liquid with a strong odor that boils at 64-65 C. Its density is 2.5 times that of air and it is decomposed by light and heat. It is very toxic by ingestion and inhalation and has been manufactured for use as a toxic suffocant by modern armies.

It is easily and quickly made by reacting sulfuric acid with carbon tetrabromide which yield the volatile liquid. Bromophosgene is also used in the commercial manufacture of crystal violet dyes and coloring agents.

Bromopicrin

also called nitrobromoform or tribromonitromethane (CBr_3NO_2) are prismatic solid crystals that are volatile and boil at 127 C (they melt at 103 C and explode violently if heated rapidly). It is used as a powerful irritant dust and military poison as well as an explosive in wartime for special applications. It was first made by mixing 10 grams of picric acid with 20 cc of Bromine and 60 grams of sodium carbonate in a liter of water and leaving it in sunlight for 5-7 days. The crystals precipitated from the water and alkali solution. They are soluble in alcohol, benzene, and ether and are made in modern industry by adding picric acid to a solution of bromine and calcium oxide in water. The solution is distilled off under partial vacuum and mild heating and the bromopicrin gas is recovered and precipitated.

Butyldichlorarsine

$C_4H_9AsCl_2$ is an oily liquid with an agreeable odor that boils at 192-194 C and is decomposed by water. It is used only as a military poison and is highly toxic by inhalation and ingestion. It is produced by reacting butyl alcohol with arsenic trichloride to yield butyldichlorarsine and dibutyl arsenic chloride.

BZ (3-Quinuclidinyl Benzilate)

is a non lethal white crystalline solid usually contained as a powder that turns to a gas when heated and which temporarily disables targets by inhalation. This causes slowing of mental and physical activity, disorientation, and hallucinations. During the Vietnam war, it was used as cluster bomb and generating pail ordnance usually delivered by aircraft and designed to heat and gassify the dust while distributing it over large areas .

The gas is a derivative of Lysergic Acid which is also used to make D-lysergic acid diethylamide (LSD). Its use was depicted in the movie Jacob's Ladder in which actor Tim Robbins plays a Vietnam veteran who, with his company, was the victim of an Army test of a hallucinogen gas intended to make the troops fearless and aggressive in the face of the enemy. In the movie, the troops attacked each other instead. BZ continues to be maintained in US military stocks as a non-lethal riot control agent.

B,B'-dichlorovinylchlorarsine

is a yellowish liquid that boils at 250 C with decomposition and has a density of 1.70. Its formula (ClCH:CH)2 AsCl is derived from the reaction of vinyl chloride and arsenic trichloride followed by reaction with acetylene which produces the toxic liquid and hydrochloric acid. The liquid volatilizes slowly and is very toxic by inhalation and ingestion and is also a very strong irritant to the skin and mucous membranes. Its only identified use is as a military poison.

B,B'-dichlorovinylmethylarsine

(ClCH:CH)2 AsCH3 is a liquid that boils at 140-150C (10mm) and is made by the interaction of acetylene and methyldichlorarsine (from the WW1 gas) in the presence of aluminum chloride as a catalyst. It is more toxic by inhalation and ingestion than its derivative and is also more irritating to the skin and mucous membranes. Its only intended use is as a military poison gas or mist.

Ethylarsenous Oxide

C2H5 AsO is a colorless oil with a nauseating garlic like odor. It oxidizes in open air and forms colorless crystals. The liquid boils at 158 C and has a density of 1.802 at 11 C. It is soluble in acetone, benzene, and ether and is used commercially for organic synthesis. It is highly toxic and is used to make other arsenic based military poisons. It is produced by the direct reaction of ethylene oxide and arsine.

Ethylchlorosulfonate

C2H5OClSO2 is a colorless oily liquid with a pungent odor that fumes in moist air. It is decomposed by water and attacks lead, tin, and copper while iron and steel are unaffected. It soluble in chloroform and ether and is insoluble in water. It has a vapor density of 5 times that of air and a volatility of 18,000 mg/cu meter. It boils at 153 C and is made by the action of fuming sulfuric acid on ethylchloroformate or by interaction of ethylene on chlorosulfonic acid. It is a very strong irritant and evolves phosgene when heated above 200 C. It is used in organic synthesis and as military poison.

Ethylene Chlorohydrin

also known as 2-chloroethyl alcohol, and glycol chlorohydrin is a colorless liquid with a faint ethereal odor. Its formula is ClCH2CH2OH and it is a deadly poisonous material that was used to make the thiodiglycol for mustard gas. The Germans did not use it as a war gas in WW1 because its odor gave it away.

It is deadly by all absorption routes and its ability to pass through ordinary protective clothing like rubber and leather to harm its targets is conferred on the mustard gas it was used to make. It is also used to make many nerve agent and pesticide compounds which will be covered in the next chapter.

Its boiling point is 128.7 C, it has a vapor density of 1.2045, and a vapor pressure of 4.9mm at 20 C. It produces vapors at 140 F (60 C) and has a bulk density of 10#/gal. Its vapors are combustible and will ignite at 797 F.

Ethylene Chlorohydrin is used in industry as a solvent for cellulose acetate, ethylcellulose, to introduce hydroxyethyl groups in organic synthesis, to cause dormant potatoes to sprout, and to manufacture ethylene oxide, ethylene glycol, insecticides, and nerve agents.

It has been manufactured by several methods, the easiest of which is the direct action of hypochlorous acid on ethylene. An earlier patented process from 1969 (Pat# 3,426,085) teaches the making of ethylene chlorohydrin by -

1. Dissolving 80 grams tellurium dioxide into 1,000 grams of hydrochloric acid 20% solution and heated to 100 C. The tellurium acts as a catalyst.

2. Ninety (90) liters of ethylene is then added which precipitates the pure tellurium which is then filtered off, redissolved, and reintroduced to the mixture.

3. The solution is reheated to 100 C and then distilled over a column and yields an azeotropic mixture of water and 42 % ethylene chlorohydrin (25 grams).

Earlier patents 2,378,104 and 2,428,590 also cover its more complex manufacture. In 1981, French scientist patented a simple method (Pat# 4,283,577) of directly mixing ethylene oxide vapor into a reactor at 50-120 C with gaseous hydrogen chloride and reacting at 130-300 C at low pressure (below 20 bars) to yield gaseous ethylene chlorohydrin which is sent to a heat exchanger to cool and then into a separation column to condense out the hydrochloric acid remaining. [Hydrochloric acid is insoluble in ethylene chlorohydrin].

Hexachloroacetone

also known as hexachloro-2-propanone, CAS# 116-16-5, Cl3CCOCCl3 is a yellow liquid made by chlorinating acetone. It boils at 204 C evolving phosgene gas as well as its own vapors that are toxic by inhalation and ingestion. It is slightly soluble in water, soluble in acetone, is combustible and is used in modern industry as a desiccant and herbicide.

Hydrocyanic Acid

has already been mentioned for its use (or misuse) by the French in WW1. During WW2, the Nazi's employed it in the gas chambers at the concentration camps as "Zyklon B" and preparations had been made for its larger scale manufacture if the decision was made to use chemical weapons during the war. It was also believed to have been used in small quantities by the Iraqi's against Iran as well as the Kurds during the 1980's. Although it is difficult to reach lethal concentrations outdoors, it is a deadly weapon in confined areas such as urban based conflicts (FIBUA- Fighting in built up areas).

Hydrogen cyanide inhibits the metal containing enzymes of the body including "cytochromoxidase" which contains Iron. Since this enzyme is crucial for providing energy to the cells (through respiration), the oxygen that is breathed in cannot be utilized and the body effectively suffocates. Symptoms include vomiting, giddiness followed by headaches, palpitations, respiratory failure, unconsciousness, and death. At very high concentrations, there may be no symptoms with sudden collapse and death.

There is no antidote to cyanide poisoning but the body can be encouraged to bind the agent in the blood while the liver produces the enzyme "rhodanese" which combines with injected sulfur (as sodium thiosulfate) to convert cyanide to thiocyanate. This is then excreted in the urine. Iron also likes to combine with cyanides and can be fixed in a trivalent from by adding sodium nitrate or dimethylaminophenol (DMAP) to form methaemoglobin which also combines with cyanides. Cobalt and B12 supplements may also help. The British army may have a pretreatment for cyanide called PAPP (para-aminopropiophenone) which actually is believed to work.

The reason that hydrogen cyanide is given so much attention here is that it is cheap and can be made in nearly unlimited volumes from the air by reacting ammonia with methane or natural gas. It is a deadly assassins poison and is still one of the most efficient killing chemical poisons known even today.

Lactonitrile

also called cyanohydrin CAS# 78-97-7, CH3CHOHCN is not a true military poison but is mentioned her in conjunction with the above. It is made by reacting acetaldehyde and hydrocyanic acid to yield a straw colored liquid that boils at 182 C. It is soluble in water and alcohol and insoluble in petroleum ether or carbon disulfide. It is toxic by inhalation, ingestion and skin contact but can be made to directly evolve hydrocyanic acid by adding alkali to the liquid. This makes it a deadly portable gas weapon for enclosed areas. It is used commercially as a solvent, and in the production of ethyl lactate and lactic acid.

Oxalyl Chloride

A well known poison called oxalic acid occurs naturally in rhubarb plants and has poisoned many grazing animals and some people. It can be made by alkali extraction of sawdust but is mass produced by reacting carbon monoxide and sodium hydroxide and distilling to yield transparent crystals that melt at 187 C for its anhydrous form and 101.5 C for its dihydrate form. Because it is very poisonous and can be produced in enormous volume from the air (carbon monoxide) and salt (caustic soda) its derivatives were explored to find a gas form that would be useful as a military weapon. The result was oxalyl chloride.

Oxalyl chloride CAS# 79-37-8, also called ethanedioyl chloride, (COCl)2 is a colorless liquid that solidifies at -12 C to a white crystalline mass that gives off carbon monoxide on reheating and decomposes to water and alkali. It is soluble in ether, benzene, and chloroform, boils at 64 C, and has a density of 1.43. It is very toxic by inhalation and ingestion and is used as a chlorinating agent in modern organic synthesis as well as being inventoried in several nation military poison gas reserves.

Oxalyl chloride is made by several processes, the most popular being the reaction of oxalic acid and phosphorus pentachloride. One of the earliest methods (patent # 2,816,140) involves heating an ester of tetrachloroethylene glycol and a carboxylic acid to between 35 and 135 C in the presence of a catalyst like activated charcoal. Oxalyl chloride is formed simultaneously with trichloroacetyl chloride. The process usually used chlorobenzene as a solvent and dimethylformamide as a catalyst and proceeded at a temperature of 100-120 C.

In the early 1980's, three new processes were patented as commercial demand for oxalyl chloride grew for its use as a chlorinating agent and in organic synthesis. The first in 1981 (Pat # 4,301,092) improved on the above process by

1. Heating 15 moles of trichloroacetyl chloride to 80-100 C.
2. Adding 6 moles of anhydrous ethylene glycol (antifreeze) over 2 hours.
3. Hydrochloric acid evolves and is distilled off, absorbed by water, and refluxed.

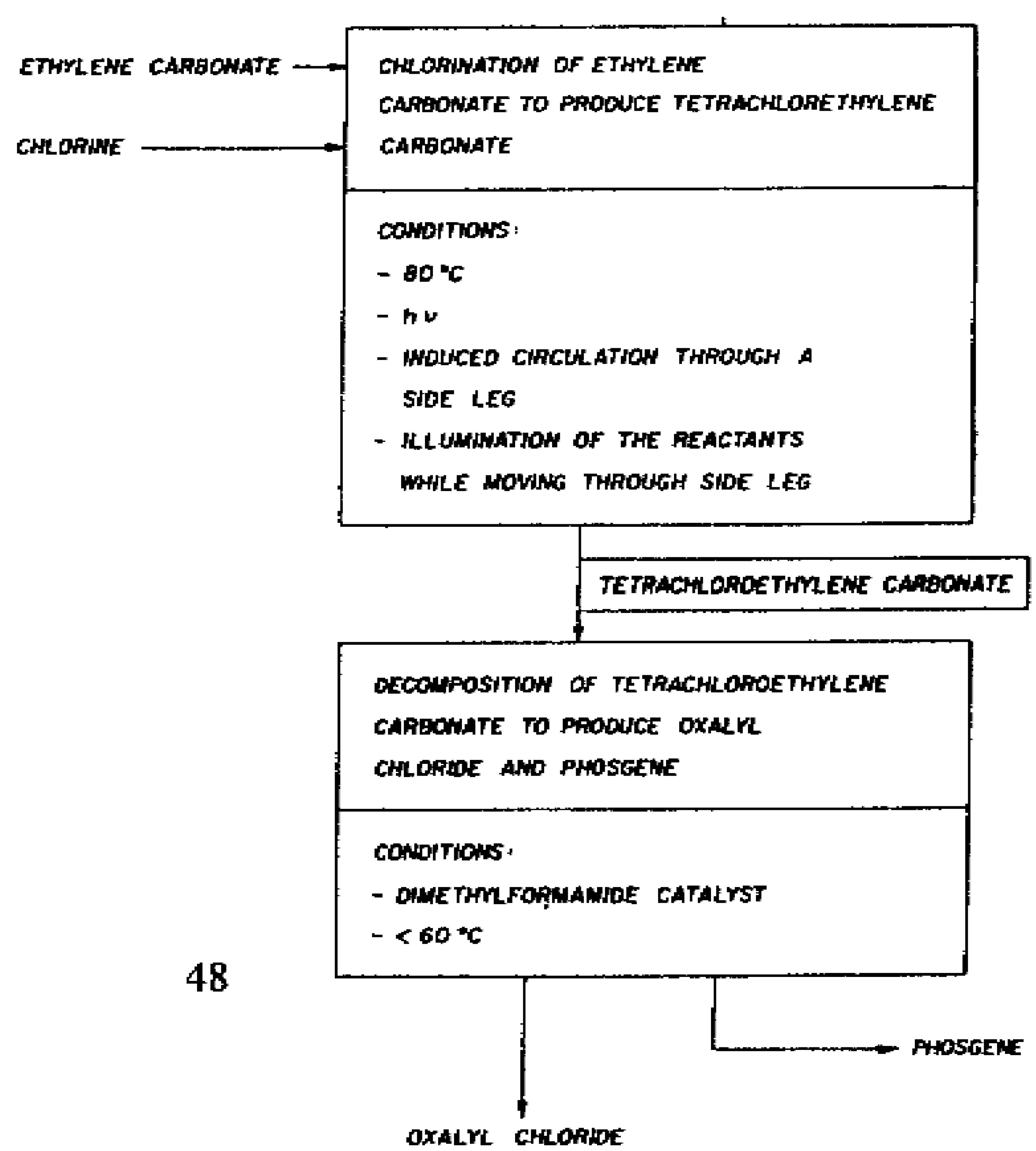
4. Chlorine is introduced at 130 C under illumination which photochemically produces hydrochloric acid (while increasing the temperature to 160 C over 8 hours) and trichloroacetyl chloride which is distilled off.
5. The mix is cooled by degassing the dissolved chlorine with nitrogen and adding the trichloroacetyl chloride (from above).
6. Triethylamine chlorohydrate is then added to yield the oxalyl chloride.

In 1982, German chemists received the more modern patent (# 4,341,720) for using phosphorus pentachloride and phosphorus oxychloride to generate the oxalyl chloride quickly and without evolving large amounts of by product gasses. These forms of phosphorus are also those used in the manufacture of the nerve agents (next chapter).

1. 1,000 parts of phosphorus pentachloride and 12 parts of triethylamine are suspended in 500 parts of phosphorus oxychloride and stirred
2. 100 parts of oxalic acid are added at 60 C and under pressure of 250 mbars over 40 minutes.
3. The temperature is increased to 70 C and stirred for 30 more minutes under pressure.

A mix of 497 parts is produced containing 20.7% by weight of oxalyl chloride and 78.4% phosphorus oxychloride is obtained by distillation with 588 parts of unreacted phosphorus pentachloride and triethylamine left over in the reactor.

The following year, Canadian scientists patented a separate process by photochemically chlorinating ethylene carbonate to form tetrachloroethylene carbonate and hydrogen chloride and then decomposing the tetrachloroethylene carbonate to oxalyl chloride and phosgene. The process is described in detail in patent# 4,390,708 and proceeds as diagrammed.



Phenarsazine chloride

also known as "Adamsite" or DM, CAS# 578-94-9, C6H4 (AsCl)(NH) C6H4, are canary yellow crystals which sublime readily. They are insoluble in water, soluble in benzene, xylene, and carbon tetrachloride. They have a density of 1.65, melt at 195C, and boil at 410C. It is made by simply heating diphenylamine with arsenic trichloride and is used as a wood treatment and as a military poison.

Adamsite acts as a nasal and throat irritating powder that induces headaches, sneezing, coughing, chest pains, nausea, and acts as a strong vomiting agent. Symptoms require about 3 minutes before taking effect and because of its high LD50 of 30,000 mg/cu. meter, it is considered safer than most tear gasses for deployment in riot control. It was disposed of by dumping into the Baltic Sea after WW2 (in 1946). Twelve years afterwards, a study of the dumping site found that virtually none of the Adamsite had hydrolyzed away and was still toxic. This and other studies would eventually lead to other means of disposal for toxic war materials.

A special riot control gas grenade was patented (#3,085,047) in 1963 incorporating Adamsite as follows.

1. 9 parts of Adamsite are mixed with 1 part of boiled linseed oil and thoroughly mixed to coat the particles with an impermeable film.

2. The particles are left to air dry on trays which stabilizes them.

3. The particles are mixed at 10-45% with 5-10% precipitated chalk (CaCO3) and 50-80% nitrocellulose fuel (propellant).

4. The dry mix is compressed into grenade cases at 1-2 tons per square inch.

The grenades instantly produce irritating gases that prevent them from being thrown back at the thrower. They also have excellent long term storage and stability and do not decay over years.

Phosgene Oxime

also known as dichloroformoxime CCl2 NOH are colorless prismatic crystals with a penetrating, disagreeable odor. With a high vapor pressure, it slowly decomposes at room temperature and accelerates with humidity. It boils at 39-40C and is soluble in water, alcohol, ether, and benzene, any of which may be used to deliver it in aerosol form. It is made by the action of chlorine on fulminic acid (HONC) or by reducing trichloronitrosomethane with either aluminum amalgam or hydrogen sulfide.

It is a strong irritant to the eyes and skin that causes instant pain like a severe insect bite. Skin surfaces become blanched in 30 seconds followed by formation of a weal in 1/2 hour. After 24 hours a brown patch forms that becomes a scab in about a weak with continuous itching while the wound is recovering. Healing usually takes up to 2 months. Because of this it is generally considered a poor mans mustard agent.

Trichloronitrosomethane

CCl_3NO is a dark blue liquid with an unpleasant odor that is soluble in alcohol, benzene, and ether, and is insoluble in water. Its density is 1.5 and it boils at 5 C (70 mm). It is a modern tear gas agent with powerful lachrymatory properties that irritate both the eyes and skin tissues. It is made by interacting sulfuric acid, sodium trichloromethylsulfinate, and sodium nitrate. The liquid slowly decomposes in solution and more quickly by itself which means it has a poor shelf life.

[A poor mans tear gas has been field improvised by college students in the 1970's by mixing two parts sodium bisulfate and 10 parts glycerin together and heating. This can be done by adding a combustible fluid or black powder and igniting it with the liquids.]

Psychotomimetic Agents

are chemicals that act on the mind interfering with normal brain activity. In the 1950's, a class of chemicals called glycol acid esters were among the first tested for this use in experiments. Very small doses were known to effect behavior severely such as causing simulated ballistic missile launches. BZ which we have earlier described, nicknamed "buzz" by the troops was the most promising. All the glycolates produce effects similar to atropine at doses at low as .5-5mg with vision, heartbeat, and salivation all affected. The worst drawback is an increased body temperature followed by hallucinations and coma in high doses which may incapacitate the recipient for 1-3 weeks after exposure. This makes the glycolates dangerous to use as a riot control agent.

Phencyclidine is a more recent development with analgesic and anesthetic properties. This material, related to PCP, causes disturbed body awareness, disorientation, and vivid dreams for several hours after exposure at 5-20 mg. At 100 mg the targets experience respiratory depression that may lead to death.

LSD was once considered a promising psychotomimetic agent but a number of those exposed committed suicide after exposure and hallucinations. Since the idea of using these as non-lethal weapons is to avoid killing the targets, it was not deemed suitable for military use.

Potential Industrial Based Military Weapons

In war, chemicals are only useful to a military force if they can be produced in volume from the available raw materials and industrial factories. Many highly toxic chemicals that may fit this description will be described in the later chapters. Here we will mention a few of that have been highlighted in the media-

PFIB stands for Perfluoroisobutylene, a gas produced as a by product in the manufacture of Teflon and related perfluorinated polymers. It is not used commercially and is made in such volumes that many nations could adapt it for large scale military use quickly. It is similar to phosgene in its toxic effects.

Flash was a reportedly new war gas used in Yemen and Afghanistan which caused death so quickly from exposure that recipients were found frozen in position in firing lines and at tables. The properties and composition of this material has never been publicly identified or described but it is possible it may have been the super toxic isomer of one of the main nerve agent groups that was produced by exposure to sunlight or ultraviolet rays. This will be described in detail in the next chapter.

Blue-X also reportedly used in the Sino-Soviet war in the late 1960's, was used to cause unconciosness. **Yellow Rain**, was also reportedly used in large scale Soviet combat but is a biologically produced chemical and will be covered in a future book.

Humanity of Chemical Weapons

Bullets and bombs directly cause great pain, injury, and suffering. Physical destruction of tissue often leads to infection and amputation of limbs, tissue, and some organs. This means that the injured individual often comes home from war with parts missing. Gas on the other hand usually kills quickly with little pain in the case of the toxic inhaled agents and nerve agents. Mustard causes serious injuries for which the pain and suffering can often be relieved before becoming too severe. This is because of the several hour delay in the onset in symptoms.

It can be argued that chemicals are a more humane way of killing and waging war and the use of chemicals has replaced more violent methods of execution of criminals in modern society such as firing squads, hangings, beheadings and so on. The arguments against this are the invisibility and near indetectability of many chemicals that kill or wound and do so without the target even being aware of it for hours. There is something in this unknown and unseen method of waging war that makes people so fearful that most would prefer to ban it.

Nations manufacture explosives and hunks of metal to propel into the bodies of its enemies in wartime. The use of science and the conversion of factories to accomplish the goal of military victory while producing the least tissue destruction is in this authors opinion the most humane way of waging war yet devised.

[Authors comments: While writing this chapter I have had the chance to consider some experiences and ideas which merit being added to this chapter.

1. In the 1970's, many college students used a vaseline coating to protect themselves from the tear gas and other chemicals used by the police and military. Although effective temporarily, the agent used would often be imbedded in the petroleum jelly and would irritate later when the individual would try to wash it off. A modern improvised method of protecting against many chemicals would be the mixing of vaseline with the appropriate chemicals the both react with the chemical agent to form less deadly salts and do not cause dermal injury or irritation themselves. The vaseline forms a water resistant, impermeable coating over the skin cells which drastically reduces the LD50's of the chemicals in the normal delivered concentrations. Chemicals in the vaseline can react with any poisons that the vaseline comes in contact with. Charcoal, bleaching compounds, and many other reactive materials are good candidates for this type of countermeasure.

2. While writing this chapter, I would spend weekends selling my own and other books at the guns shows. Before the Houston show in August 1997, I checked into the Motel and before I could carry my bag up to my room on the 2nd floor, two kids had already opened the door to my van and were carrying off my cheap $20 radio and CD's. I considered booby trapping the vehicle to prevent any further misappropriation's of my property, but I didn't have anything in the van that I could use that wouldn't kill them. I then pondered the possibility of using my advance chemical knowledge to make a non-lethal booby trap that would protect, deter, and result in a measure of justice. Such a trap would propel a dye that would permanently stain all clothing and skin tissue and brand the individual as the culprit. I would also incorporate an extremely irritating industrial odor generating material that is used to warn people away from deadly poisonous materials and leaking gas. Some of these in tiny concentrations make skunk odor seem pleasant. I would of course, use it undiluted. This would make it easy to trace the culprit and would also extract a measure of justice. It would also be good option for non-lethal shotgun shells.

The only problem with the above idea is that it also permanently stains and marks my own property and it would be possible that I would forget I had the trap in the on mode and "nail" myself. With my luck, I would probably be sued by the robber for inflicting psychological discomfort on the thief and end up having to work supporting them instead. Because of this and the Bernie Goetz experience it is probably better just to kill em off. This could easily be done by leaving an exposed wire in my van around the stereo (I have a 110 volt system in the vehicle). There is still the problem of forgetting I have it turned on!

One final comment I wish to make is that it became apparent to me that there were many generic recipes that permitted the manufacture of many of these chemicals form off the store shelf items. Mustard gas can be easily made in volume by anyone who can make moonshine. These ideas seemed to fit the plan I had for this book but it became apparent that if 2 tons of mustard had been used in Oklahoma City instead of explosives, the results would have been far more deadly. For this reason, I have avoided detailed instructions for many of the chemicals and devices in this book. Don't worry, it will still scare the hell out of them anyway.]

Simple Lung Injurants

Dichlordimethyl Ether [$(CH_2Cl)_2O$] was first used by the Germans in January 1918 and was designated "X". It is made by directly chlorinating methyl ether (Which is made by dehydrating methanol).

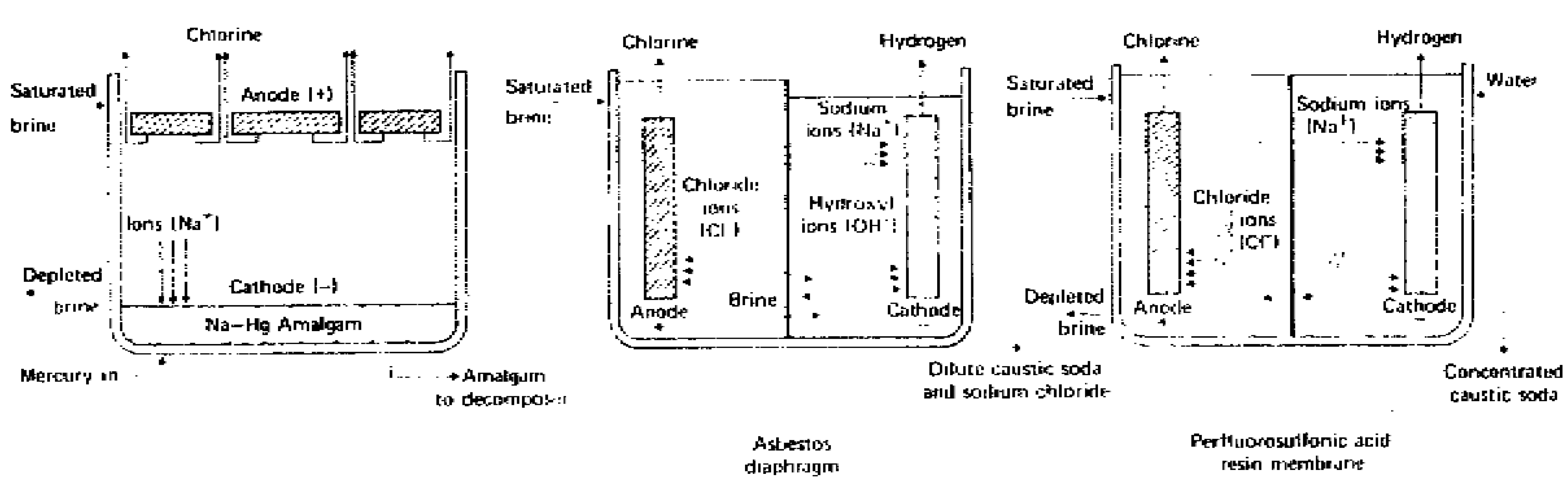
It is a colorless liquid that boils at 221 F (105 C) and has a specific gravity of 1.37. Its volatility is .18 mg/ liter, it irritates at .015 mg/ liter, is intolerable at .04 mg/ liter, and is lethal at .47 mg/ liter in 10 minutes. It is easily decomposed by water which makes it easy to decontaminate an area quickly.

The original purpose was to increase the volatility of ethyldichlorarsine and was used in combination with it. It has the typical lung injurant properties as well as a unique ability to damage the labyrinth of the ear so that the target reels and staggers and cannot maintain body balance. This and Dibromomethyl ether were classified by the allies as "Labrynthic Substances" and have a unique place by themselves among war weapons because of this property. Armies can now make the enemy too dizzy to stand up and fight them.

Dibromdimethyl Ether [$(CH_2Br)_2O$) is made the same way as dichlordiethyl ether, only the methyl ether is brominated instead with bromine. It has a higher boiling point of 155 C (221 F), and lower volatility of .022 mg/ liter. It is also less irritant needing .022 mg / liter and it becomes intolerable at .05 mg/ liter. It is more toxic and kills in 10 minutes at .04 mg/ liter and is denser at 2.2 specific gravity.

It shares the same labrynthic properties as dichlormethyl ether as well as its lung injurant effects. Both these materials have considerable value as weapons of war.

Chlorine gas [CAS#7782-50-5] existing as Cl or Cl_2, it is one of the largest volume chemicals produced in the world, and as you have already seen, it is widely used in chemical weapons. Almost all of it is produced by electrolysis of sodium chloride. We taught how to do this in the field in Vol's 1,3, and 4 in converting salt to chlorates with a car battery. The process is basically the same here except that the sodium which is drawn to the cathode and the chlorine which collects around the anode are both drawn off continually as shown in the three different types of cells below.



The chlorine gas is collected, compressed to six atmospheres which turns it to a liquid, and stored, or scrubbed into water and stored in solution where it forms hydrochloric acid. When it is a liquid, it has a specific gravity of 1.46 and when it is a gas it is 2.5 times as heavy as air so it will cling to the ground as it travels with the wind. Its gas is greenish yellow with a pungent odor and caustic characteristics. The liquid produces 434 times its volume in gas at 25 C and it evolves easily from its storage since it boils at -28.5 F (-33.6 C). This made it easy to use from gas cloud cylinders in WW1. It is only slightly soluble in cold water which offers a way of separating it after scrubbing.

Chlorine gas is one of the most reactive substances known when mixed with moisture. It attacks almost all metals and organic substances. Anhydrous chlorine does not attack metals and can be stored when completely dry. It is classified as a lung injurant but it also affects the eyes and the mucous membranes of the nose , throat, larynx, and pharynx. It kills by producing spasms and pain in the muscular walls of the bronchi, narrowing their lumen and causing gasping for breath. If the target can get away from the gas, the spasms soon relaxes and breathing becomes easier. The gas also irritates the bronchial tubes which produce an inflammatory exudate that may obstruct them. The pulmonary air sacs may be directly damaged and fill with blood causing suffocation, and finally, a disruptive emphysema may occur from the continuous coughing and rupturing of the alveolar cells which allows passage of air into the lung and neck tissues. This interferes with normal respiration and leads to asphyxia.

Chlorine is lethal at 2.53 mg/ liter for 30 minutes and at 5.6 mg/ liter in 10 minutes. It is non persistent and lasts for only 5-10 minutes in the open air, it is effective in this short time span and is extremely volatile (19,369 mg/ liter). It has a specific gravity of 1.4 and vapor density of 2.5.

It can be mass produced in virtually unlimited quantities and is very easy to manufacture. It is stable when anhydrous and does not decompose from explosive shock or heat. All these characteristics combine to make it a desirable and effective war gas. The main disadvantage is that, because it is so reactive, it can easily be reacted with many materials in gas mask filters and canisters which makes it easy to defend against, which is exactly what happened in WW1. Once it was no longer effective, the search was on for ways to defeat the gas masks. Chlorine was called "Bertholite" by the French, "Chlor" by the Germans, chlorine by the English, and designated Cl by the Americans.

Because of its enormous volumes of supply, the search soon began for other chlorine based chemical weapons that could be used in war. It is manufactured and sold in enormous quantities worldwide for use in swimming pools and making a huge range of chlorinated compounds and plastics, processing meats and fish, flame proofing materials, and water purification.

Methylsulfuryl chloride [CH_3OSO_2Cl] was developed quickly by the Germans to be used in artillery and mortar shells. The chlorine was too volatile and could not be loaded into shells. You cannot use gas from cylinders if the wind is blowing against you because it just blows back into your face. If you can launch gas shells at ranges of 1/4 to 15 miles with artillery, it will dissipate in the air before it reaches your own lines. By April 1915, the Germans introduced their first lung injurant, also known as Methylchlorosulfonate.

It is a colorless, viscous liquid with a specific gravity of 1.492, boils with decomposition at 134 C, and has a vapor density of 4.5 which allows it to hug the ground much like chlorine. It lacrimates at .008 mg/ liter (one part in 750,000), is intolerable at .05 mg/ liter, and is fatal in 10 minutes at 2 mg/ liter. It causes death by producing edema similar to that of chlorine and phosgene which results in the target drowning in their own blood. Its volatility at 20 C is 60 mg/ liter.

It is produced by the direct action of sulfuryl chloride on methyl alcohol and is used commercially in organic synthesis today. (Sulfuryl chloride is made by mixing sulfur dioxide and chlorine in the presence of activated charcoal)

Ethylsulfuryl Chloride [$ClSO_3C_2H_5$] is made the same way as methylsulfuryl chloride above using ethyl alcohol in place of the methyl alcohol. This was the French counter to the German version and was used in shell fillings as "Sulvanite".

It is a colorless liquid with a specific gravity of 1.44 and boils with some decomposition at 275 F (135 C). Its vapors lacrimate at less than 1 ppm and it is intolerable at .05 mg/ liter. At 1 mg/ liter it is fatal in 10 minutes. It is less volatile, but more lacrimatory and toxic than methylsulfuryl chloride. Neither was used very long as a lung injurant as the race continued for deadlier and more effective war gases.

Chlormethylchloroformate [$ClCOOCH_2$] was called "Palite by the French, and K-Stoff/C-Stoff by the Germans. It was produced by first mixing methyl alcohol with phosgene to produce methylchloroformate. The reaction as follows $COCl_2 + CH_3(OH) = ClCOOCH_3 + HCl$. This was then chlorinated in the presence of strong light forcing the chlorine to progressively replace the hydrogen atoms in the methyl group. Both the mono and di forms are produced. It is now made by chlorinated methyl formate.

This process yielded a clear liquid with a specific gravity of 1.48, it boils at 109 C (228 F), and has a vapor density of 4.5. It has an ethereal odor and is attacked by alkali's evolving formaldehyde, carbonic acid, and hydrochloric acid. Its vapor pressure is 5.6 mm at 68 F.

At .0528 mg/ liter it causes slight lacrimation and becomes lethal at 1 mg/ liter in 30 minutes. Because it is about 5 times as toxic as chlorine making it a great improvement but was soon displaced by phosgene and chlorpicrin. It was used in trench mortars and projector bombs.

Dimethyl Sulfate [CAS#77-78-1] $(CH_3)_2 SO_4$, also known as D-Stoff by the Germans and Rationite by the French, was used incidentally in early German artillery shells with the primary ingredient of methylsulfuryl chloride. No one at the time realized how deadly this material actually was. It was a good lacrimator, powerful vesicant, and was very toxic. The French soon realized the value of these properties and adopted it as ordnance filling in 1918.

Dimethyl Sulfate is manufactured by treating a solution of "Oleum" (Fuming Sulfuric Acid) with methyl alcohol. This is distilled off in vacuum (a vacuum pump pulls off all the gas and atmosphere leaving a low pressure to speed the production of further gas) and condensed. Before WW1 it was used (including today) for methylating amines and phenols. It is also used today to make polyurethane adhesives. Modern production reverses the order with the Oleum added slowly to the methanol.

It is a colorless oily liquid that is soluble in ether, alcohol, and water. Its density is 1.3516, it boils at 188 C with decomposition and is also considered a combustible vapor. At 68 F its volatility is only 3.3 mg/ liter which is low for being a lung injurant but high as a vesicant. It is decomposed by the water vapor in the air forming sulfuric acid making it limited in its persistence. This makes it useful on the tactical offensive but limited in effect.

As a vapor or mist, it irritates the conjunctiva and respiratory system and it is directly toxic to the lungs resulting in bronchitis, pneumonia, and lung edema from the formation of sulfuric acid on the tissues. In 10 minutes, a concentration of .5 mg/ liter is fatal making it almost as toxic as phosgene. In lower doses it produces an analgesia of the skin which lasts up to six months after exposure which is why it is also a vesicant agent, and it is also a carcinogen when absorbed through the skin in low doses and produces tumors in lab animals.

Perchlormethylmercaptan [CAS# 594-42-3] $SCCl_4$ also known chemically as trichloromethylsulfenyl chloride and during the war as carbon tetrachlorsulfide by the French who first used it at the Battle of Champaigne in September 1915. It was the first chemical used in a gas artillery shell by them. It was made by directly chlorinating methylmercaptan (CH_3SH), or carbon disulfide with a small amount of iodine as a chlorine carrier. It is also made in modern manufacture by chlorinating thiophosgene or methyl thiocyanate.

It is a light yellow, oily liquid with a disagreeable odor and a specific gravity of 1.71. It boils at 149 C (300.2 F) yielding a vapor 6.5 times as dense as air. It is insoluble in water and is slowly decomposed by moist air, iron, and steel, reducing and oxidizing agents, and chlorine. It is immobilized completely by charcoal in gas masks making it ineffective against them. Its volatility is 18,000 mg/ cu. meter making it able to achieve large concentrations in air.

The vapor lacrimates at .010 mg/ liter and is intolerable at .07 mg/ liter. It is lethal at 3 mg/ liter in 10 minutes making it about 1/6th as toxic as phosgene. Its low toxicity caused it too be quickly abandoned. It is used in industry as a dye intermediate and as a fumigant.

Phosgene [CAS# 75-44-5 COCl2] was known as Collongite by the French, D-Stoff by the Germans, and designated CG by the British and Americans. Its other chemical names are carbonyl chloride, carbon oxychloride, and chloroformyl chloride. It was the second toxic gas to be used in large quantities in the war. First used by the Germans on Dec 19th, 1915 when 88 tons were released from 4,000 gas cylinders, it produced 1,069 casualties with 120 deaths. The French soon retaliated and it became the primary battle gas for the allies for the rest of the war. It was used by both sides in enormous amounts and caused over 80% of the gas fatalities in the war.

Phosgene was first discovered in 1812 by the British chemist John Davy who mixed carbon monoxide with chlorine in the presence of sunlight which acted as a catalyst to speed up the reaction. In WW1, both sides would set up huge factories to produce the carbon monoxide which was then reacted with chlorine in the presence of animal charcoal which produced the phosgene. The gas was passed through a sulfuric acid scrubber to remove any moisture where it would then be cooled into a liquid for storage in tanks. In modern production, standard charcoal is used as a catalyst. An improvised method for making Phosgene involves the direct mixing of carbon tetrachloride and sulfur trioxide (oleum) which yields phosgene and chlorosulfonic acid. Although this is not a good yield, it makes it easy to produce a binary weapon such as a gas grenade with plastic or ceramic lining that dispenses the vapors on mixing immediately.

Phosgene is a colorless and odorless gas that is easily liquefied under pressure. Its odor is similar to freshly mown hay in dilute concentrations. It boils at 8.2 C (46.7F) making it hard to use in cold weather. Its rate of evaporation was so slow that it was mixed into chlorine gas 50/50 where it would speed its volatilization. It was used in cloud gas attacks in this mixed form. It is slightly soluble in water and is quickly broken down by it which is how it causes injury. When it mixes with water, it forms hydrochloric acid and carbon dioxide which mixes into the respiratory tissues causing corrosion and inflammation. The irritation it produces causes men to breathe it in more deeply resulting in greater and deeper exposure. The effects of the injuries take several hours to appear when the lung injuries began to cause bloody fluids in large amounts. Eventually, the lungs cannot keep up with the demand for oxygen and even the slightest physical exertion often resulted in death. These effects are slowest in the trachea and bronchi where there is less moisture to react with and produce the acids. Phosgene is soluble in benzene and toluene and its specific volume is 3.9#/ cu. ft.

It is widely used in modern industry to produce isocyanates, polyurethane and polycarbonate resins, carbamates, pesticides, and dyes. It is heavier than air and must be stored in dry conditions so it does not convert to acid which attacks metal containers and weapon parts. The main reason for its effectiveness in the war is that the men breathing it did not realize they had been gassed. The only easily distinguished effect that was quickly noticed was its effect on tobacco smokers who would experience a flat metallic taste from their cigarettes and especially their pipes. The phosgene is very stable chemically if dry and can be stored indefinitely. It does not react from the heat of explosions and is ideal for use in explosive shells and bombs which heat and disseminate it as a vapor. Its specific gravity is 1.38

Di-Phosgene [ClCOOCCl3] known chemically as trichloromethyl chloroformate, as Perstoff by the Germans and Surpalite by the French, it was first used by the Germans at Verdun in May 1916 in retaliation for the French use of phosgene in artillery shells in Feb. 1916. It is a colorless liquid with an odor similar to the new mown hay like phosgene. It is decomposed by heat, activated carbon which yields phosgene, by alkalis, and hot water. It is soluble in alcohol, benzene, and ether. Its vapor density is 6.9 making it much heavier than air and it boils at 127 C whereby it gives off its persistent vapors that hug the ground for 30 minutes or more. At 20 C (68F) its volatility is 26 mg/ liter. On contact with moisture in the body tissues it yields two molecules of phosgene followed by the conversion to carbonic and hydrochloric acids.

Because of its high boiling point, the soldiers in the field could fill artillery shells with diphosgene and needed only a gas mask to protect them. The shells were then cemented shut for immediate use. This gave the Germans a large material handling advantage since the allies shells had to be filled and sealed under dangerous conditions far from the front. Diphosgene has about the same toxicity as phosgene but will persist in the field for up to 30 minutes where phosgene often dissipated in 10 minutes. It is also twice as heavy as phosgene making it more effective in close to the ground concentrations. This made it the most effective "killing" gas in the war.

Diphosgene is made by

1. Chlorinating methyl formate
2. Chlorinating methylchloroformate

The methylchloroformate is made by reacting phosgene with methyl alcohol in the presence of calcium carbonate. This is then reacted with chlorine in ultraviolet light or with electricity as in electrochemical cells. The German chemists observed that by completely chlorinating alcohol esters of formic acid that they became less lacrimatory and more toxic.

Toxic Lung Injurants and Sternutators

Phenyldichlorarsine [CAS# 696-28-6 $C_6H_5AsCl_2$] also known as Sternite by the French and Blue Cross #1 by the Germans, it was the first toxic lung injurant to be used when the Germans introduced it in September 1917 where they used it as a solvent for , and in combination with 40% diphenylcyanarsine. It also had the desired sternutator property of penetrating the gas masks up to this time and by causing vomiting, nausea, and coughing as well as other irritation to the upper respiratory tract, it would cause the defender to remove his mask so the other gases could work. It also has vesicant properties where it can blister all tissues in which it comes in contact with. This combined with the fact that it carries arsenic into the lungs and skin tissues making it a direct poison, makes it one of the most effective and deadly war gases. It blinds very quickly when used in concentration.

It is a microcrystalline solid at -20 C and boils at 256 C. Its volatility is 404 mg/ cu meter and its vapor pressure is only .00146 at 59 F. When it is heated to near boiling, it produces dense vapors from its clear, viscous liquid that is 7.75 times as heavy as air. It is insoluble in water and is quickly dissolved into alcohol, ether, and benzene.

Its toxicity is greater than that of phosgene in which a dose of .26 mg/ liter is fatal in 10 minutes. Its blisters are less damaging and slower to form than mustard gas (30 minutes or more) and usually heal more quickly. Death is usually caused by pulmonary edema. Despite all these effective properties, it was primarily used as a solvent and gas mask penetrator in combination with other toxic poisons. The combination mixtures were easy to fill into shells and did not yield significant vapors until heated from the shell explosions. It would decompose when exposed to moisture and wet clothing gradually.

Phenyldichlorarsine is made by heating phenylmercuric chloride and arsenic trichloride together at 100 C.

Ethyldichlorarsine [CAS# 1789-58-8 $C_2H_5SiHCl_2$] also called "Dick" by the Germans, it was first used in March 1918 with the idea that it would be more volatile and non persistent than mustard gas as well as more lasting in its effects than either mustard or phosgene. It was planned for use for the grand offensive of 1918 to support their infantry attacks.

It is a powerful respiratory irritant and if only small amounts were breathed in before a gas attack, the exposed troops could not keep their masks on. At only one part in two million it irritates the throat and at one part in 500,000 it burns the chest for about an hour after exposure ceases. Its first use as a vesicant was poor and it did not damage the skin as much as expected when short exposures of 5 minutes or less occurred. Longer exposures were more effective, but its potent toxic properties made it ideal for use a toxic lung injurant. At .01 mg/ liter it is intolerable due to its irritating effect on the nose and throat in one minute and is lethal at .5 mg/ liter in 10 minutes, and .1 mg/ liter in 30 minutes. This is over 3 times the toxicity of phosgene for longer exposures. It produces pulmonary congestion, edema, and pneumonia while simultaneously being rapidly absorbed and directly and quickly poisoning the body with organic arsenic.

The German chemists manufactured ethyldichlorarsine by

1. Mixing sodium arsenate with ethyl chloride under pressure and heat.
2. The sodium arsenate produced in step one is then treated with sulfurous acid to reduce it to ethyl arsenous oxide.
3. This is then reacted with hydrochloric acid to yield the final ethyldichlorarsine.

Modern production involves direct chlorination of the ethyl arsenous oxide. The material is a colorless mobile liquid that boils at 156 C with decomposition and turns yellowish in when exposed to light and air. It is soluble in alcohol, benzene, ether and water and is 6 times as dense as air. Its volatility is 20,000 mg/ cu meter at 21.5 C. When broken down by moisture, its hydrolysis product - ethylarsenous oxide - is also poisonous when swallowed. It is also broken down by oxidizers.

Phenyldibromarsine $C_6H_5AsBr_2$ is made by brominating phenylmercuric hydroxide and then heating it with arsenic trichloride under pressure. This yields a colorless liquid that boils at 285 C with slight decomposition and it has a density of 2.1 at 15 C. When dispersed by the heat of an exploding shell, the vapors were slightly lacrimatory and partly sternutatory. Its toxicity was .2 mg/ liter in 10 minutes making it the most lethal form of organic arsenic used in WW1. It was introduced by the Germans in September 1918 and was not used widely enough to evaluate its effectiveness in the war.

The other Sternutators

Diphenylchlorarsine [CAS# 712-48-1] $(C_6H_5)_2$ AsCl was introduced by the Germans in 1917 who called it "Clark 1" and used with mustard gas with the idea of penetrating the allies gas masks which until then had stopped all the lung injurants. This material was dispersed as a dust on the battlefield which was not absorbed by charcoal or sodium carbonate in the gas filter cartridges.

It was discovered in 1881 and the Germans used a complicated process based on their available raw materials using

1. Sodium arsenite to treat benzene diazonium chloride to form sodium phenylarsenate.
2. This was reacted with hydrochloric acid to yield sodium phenylarsenate.
3. This was reduced to phenylarsenous acid by treatment with sulfur dioxide and water.
4. This was treated with sodium hydroxide to form sodium phenylarsenite.
5. This was treated with benzene diazonium chloride which converts it to Sodium Diphenylarsenite
6. This is treated with hydrochloric acid to form diphenylarsenic acid.
7. This acid is reduced to diphenylarsenous oxide by treating with sulfur dioxide and water.
8. This is converted to diphenylchlorarsine by chlorination with hydrochloric acid.

Modern production is easily accomplished by reacting benzene and arsenic trichloride and heating them together with an aluminum chloride catalyst.

Diphenylchlorarsine is composed of colorless crystals which turn into a dark brown liquid which becomes semi-solid and decomposed slowly by water. It is soluble in carbon tetrachloride, chlorpicrin, phenyldichlorarsine, and other organic solvents. It is almost insoluble in water which decomposes it rapidly and yields hydrochloric acid and phenylarsenic oxide which is also toxic. The crystals have a specific gravity of 1.4, melt at 45 C (113 F), and boils with decomposition at 383 C (720 F). As a solid its vapor pressure is negligible and its volatility is only .00068 mg per liter at 20 C.

The diphenylchlorarsine is volatilized by heat and the Germans attempted to use the heat from the explosion of artillery shells bursting. The vapors it forms condense in the air into very fine solid dust particles and mist clouds. The heating is important because it will not form the toxic clouds without it. The artillery shells were not hot enough to form the vapor that recondenses and this resulted in large and mostly ineffective particles applied on the battlefield. They also placed the explosive around the chemical which compressed them instead of blowing them apart into finer particles which also detracted from the effectiveness. The allies quickly conducted several experiments and learned to use heat distillation to disperse the agent on the battlefield which made it much more effective on the battlefield. This technical mistake by the Germans proved very costly to them as they expended over 14 million ineffective artillery shells with this bad design.

Diphenylchlorarsine is pulverized to a powder and can be dispersed with a high temperature bursting charge in an artillery shell, bomb, or thermally distilled as a toxic smoke. This breaks it up into microscopic particles that float in the air and easily penetrate gas mask canisters where they pass through the filters and into the respiratory tract. At 1 part in 25 million it produces irritation to the throat while at 1 part in 10 million it becomes unbearable in 1 minute. 1.5 mg/ liter is lethal at 10 minutes and .6 mg is lethal in 30 minutes. . The volatility of diphenylchlorarsine is so low that it is impossible to reach effective concentrations of vapor in the air but the dust and mist are effective and can reach very high concentrations in air.

At low concentrations the irritation tickles the nose followed by sneezing and flow of mucous similar to a bad cold. This spreads down the throat which causes coughing and choking until the lungs are affected. Headaches begin and become unbearable with sensations of pressure in the jaws and the teeth. Retching and vomiting can also occur with vertigo, trembling, and weakness. At higher concentrations they become completely unable to walk followed by giddiness, fainting, and loss of conciousness. Systemic arsenic poisoning begins with all the associated symptoms. The symptoms slowly disappear if uncontaminated air is reached.

Diphenylchlorarsine is also absorbed through the skin, however the concentrations achieved on the battlefields of WW1 resulted in few deaths. It remains a theoretically potent weapon and has been included in some modern munitions reserves. The US maintains stocks using the designation DA and it is intended for crowd control at low concentrations.

Diphenylcyanarsine [$(C_6H_5)_2AsCN$] known as Clark II by the Germans who first used it in May 1918 and designated as DC in modern US inventories, it was intended as a replacement for diphenylchlorarsine with the idea that it does not decompose in water and it also proved to be more physiologically active than its predescessor. It is the most powerful irritant compound used in the war and is intolerable at only .00025 mg/ liter concentration making it 4 times as powerful as diphenylchlorarsine. Its toxicity is only 1 mg/ liter in 10 minutes making it 50% more toxic. These toxic levels were typically not attainable in battlefield conditions and it produced few casualties but it easily penetrated the gas masks of 1917-18 and incapacitated large numbers of troops during artillery bombardments. This made it easy for the German troops to overrun the bombardment areas. The irritation forced many soldiers to remove their masks causing lethal exposures from the lung injurants that were simultaneously delivered.

Diphenylcyanarsine was made by reacting potassium or sodium cyanide dissolved in solution with diphenylchlorarsine. The chlorine is exchanged with the cyanogen as follows -

$$(C_6H_5)_2AsCl + NaCN = (C_6H_5)_2AsCn + NaCl$$

A solid colorless crystal is formed that melts at 31.5 C (91 F) and boils with decomposition at 350 C (662 F) and produces a vapor 8.8 times as heavy as air. It smells like garlic and bitter almonds.

DC (called CDA during the war) was by far the most effective harassment agent of the war and was rapidly employed by both sides in counterbattery fire to stop enemy assaults. It always forced the donning of gas masks even when a few shells were used and always hampered the enemies efforts. The British developed a true candle that would distill off a toxic smoke of DC which could be delivered instead of artillery shells and was far more effective. The toxic smoke produced by the heated mass was 100 times more effective than the dust cloud. Had it been kept secret and effectively deployed in volume it could have influenced the outcome of the war by itself. DC affects humans at only 1:35,000,000 parts of body weight making it one of the most powerful irritants ever invented.

Ethylcarbazol [$(C_6H_4)_2NC_2H_5$] was the last of the irritants used by the Germans in the war. It is a white flaky solid that forms leaflet crystals and melts at 68 C (149 F). It boils at 175 C (5 mm) producing a vapor 7 times heavier than air. It is soluble in ether and hot alcohol and is insoluble in cold water and is not decomposed by it. It was not intended as an irritant, had only a small effect, and was primarily used as a solvent for the arsine compounds.

It is used in modern industry for dyes, pharmaceuticals, and agricultural chemicals. It is made by reacting ethyl chloride with potassium carbazole.

Diphenylaminechlorarsine [CAS# 578-94-9, C_6H_4 (AsCl) (NH) C_6H_4] was invented independently by both the Germans in 1915 where they decided not to use it because it decomposed on heating, and by an American officer Major Roger Adams. It would be named after him and was called Adamsite. [The modern "Adamsite" will be discussed later in the chapter]. The US and British efforts focused on finding a chemical similar to diphenylchlorarsine that was much simpler to make. They simultaneously discovered this new compound with only a slight chemical difference but was much easier to manufacture. It was made by mixing and heating together diphenylamine and arsenic trichloride. Diphenylamine was already widely used in the dye industries and arsenic trichloride was simply made by chlorinating white arsenic (As_2O_3).

When first manufactured, the Adamsite is a dark green molten mass that is purified by dissolving in benzene and recrystallizing from glacial acetic acid. The canary yellow crystals produced melt at 195 C and boil with decomposition at 410 C. It is insoluble in water and soluble in carbon tetrachloride and xylene. It is unaffected by humidity and is very stable. It slowly hydrolyzes in water yielding hydrochloric acid and a toxic arsenic oxide. It is also much less flammable than diphenylchlorarsine and can be easily dispersed by artillery bursting charges. It attacks and corrodes metal so the shells must be lined. It persists in air about 10 minutes in all weather so it is considered a non-persistent agent.

The symptoms it produces are very similar to diphenylchlorarsine except they appear more slowly and last about 3 times longer. Where diphenylchlorarsine incapacitates for about an hour, the Adamsite lasts for 3 hours making it more efficient at putting enemy troops out of action for longer periods. It is odorless and the targets do not know they are breathing it until it produces physiological effects. It irritates at concentrations as low as one in 30 million and is lethal at .65 mg/ liter in 30 minutes or in 10 minutes at 3 mg/ liter.

It is most effective when delivered as a smoke but when atomized by explosion or distilling it easily penetrates the gas mask filters and plugs the filter media making it harder to breathe. It has been widely used to suppress riots and has been mixed with tear gas in hand grenades where it distills off with progressive burning and is in its most irritating form.

Vessicant Agents

Mustard gas, also known as Dichlorethyl Sulfide or Dichlorodiethyl sulfide [$S(CH_2CH_2Cl)_2$] was called "Lost" by the Germans, "Yperite" by the French, and Mustard Gas by the British and Americans. It was first used in battle on the night of July 12, 1917 in an artillery bombardment by the Germans against the British at Ypres. It stunned the allies and produced thousands of casualties before any defense at all could be improvised. A new and deadly form of chemical war had begun.

Up until this time the main battle gases were lung injurants that attacked the respiratory tract and had to be inhaled to work. By the summer of 1917, the gas masks had finally been made so effective that they could no longer be penetrated and the only casualties being produced were those who couldn't get their masks on and adjusted before breathing the gas. The German chemists needed to find a chemical that would penetrate the mask, plug it and force them to remove it, or attack another part of the body so that a mask would not matter. They found the solution simultaneously when they introduced Blue Cross, the diphenylchlorarsine that would penetrate the masks of 1917, and mustard gas which they mixed and delivered with it. The mustard agent would terribly burn any part of the body it came in contact with and its vapors easily penetrated leather boots and even rubber clothing. As well as being a powerful vesicant, it was also very toxic and would kill when breathed in tiny amounts. There was no defense against it at all and it became the king of all the battle gases of the war. It was so effective that it was stockpiled by both sides in WW2 and is even included in modern munitions inventories of all the major powers even today.

Mustard gas was first delivered by artillery shells which burst in the air producing an invisible cloud that spreads over the battlefield. Its heavy vapor (5.5 times as dense as air) is nearly odorless in field concentrations and in strong doses smells like horse radish or mustard. It is a transparent oily liquid with a specific gravity of 1.27 which boils with slight decomposition at 217 C (422.6 F). It would turn into white solid crystals at 14 C (57 F) so the Germans dissolved it into another solvent to lower its freezing point. This combination made the mustard gas attacks almost impossible to detect. It could permanently blind at concentrations below that which people could smell it and was invisible when distributed by shells. The troops had no idea they were even being gassed until they began to show symptoms 1-2 hours later.

The vapors initially produce no irritation to any part of the body. With no discomfort, the troops went about their business breathing in the gas and getting it on their skin and clothes. Some of the troops would sneeze when some of the vapors would precipitate as a powder and irritate the nose. In 1-2 hours, the eyes were inflamed and the troops began vomiting. The skin began to blister and the troops finally knew they had been gassed. By the time the troops could be evacuated most of them were blind and had to be led to the evacuation stations. In a short three week period the Germans caused enormous casualties with their bombardments which continued until July 1918 when they began to run out of mustard agent.

In only three months they produced over 160,000 casualties of which only 1,859 were killed. By the end of the war 12,000 tons of mustard agent would injure or kill over 400,000 allied troops. This was one casualty for every 60# of mustard used. Before this it took about 230# of chemicals to cause a casualty with lung injurants and this was about to become much harder to do with the improved gas masks. Germany, in the summer of 1917 was facing the combined economic and military might of the whole world and would never have survived the onslaught if not for the German chemists who were able to mass produce for the army, the massive amounts of yellow cross (mustard gas) shells which now shielded Germany from all the allied advances.

Mustard was a known chemical before the war. In 1860 it was prepared by passing ethylene into sulfur dichloride. The scientists who developed it described its vapors as causing the most serious destruction to the body parts it comes in contact with. In 1886, a German chemist discovered a new way to make it by reacting hydrochloric acid with thiodiglycol. With the data in hand, the Germans secretly began to make it in quantity in the spring of 1917 and were so happy with the initial production results that they began to mass produce the yellow cross shells with mustard as the filling and were able to build a large inventory before the allies were even aware of it.

Mustard gas has a low volatility and this makes it persistent in the areas it is used. It can last a day or more in the open to a week in the woods during the summer. In the winter it can last several weeks wherever it is applied. Because of this is cannot be used on the tactical offensive because you cannot send troops into the area you have just gassed. On the defense it is a tremendous weapon which prevents foot movement over any area that has been saturated with even tiny amounts of mustard. Some soldiers in the war carried small amounts of liquid mustard on their clothing into "safe" bunkers only to find they had gassed all the occupants in a couple of hours unknowingly. The volatility of Mustard Gas is described in the following chart.

Temperature		Vapor Pressure	Volatility
C	F	mm Hg	mg./ liter
0	32	.026	.250
5	41	.030	.278
10	50	.035	.315
15	59	.042	.401
20	68	.065	.625
25	77	.100	.958
30	86	.150	1.443
35	95	.222	2.135
40	104	.450	3.660

The Germans used two different production processes for mustard during the war and both were successful because the raw materials were abundant and easily mass produced. The basic raw materials for both processes included ethyl alcohol which was used to produce ethylene, sodium sulfide, sulphur, and chlorine.

Mustard is rapidly dissolved in organic solvents like ether, chloroform, and acetone. It can also be dissolved in all the vegetable and animal fats but is hard to dissolve in waxes, mineral oil, and vaseline. It is soluble in gums and rubber which is one reason it so easily penetrates rubber clothing. It also penetrates into almost all kinds of fabric and clothing and are carried by it anywhere the wearer happens to walk or drive to. These properties of penetration, solubility, invisibility, and persistence are why it is so deadly a chemical agent. It is very hard to defend against.

Mustard gas is lethal at .15 mg/ liter in 10 minutes and .07 mg/ liter in 30 minutes. At .001 mg/ liter for one hour it will blind the victim making them a casualty. Mustard is five times as toxic as phosgene. Because there was no means of detecting it in WW1, the mustard caused injuries at dosages much smaller than this in 2-4 hours without anyone realizing they were even exposed. This resulted in thousands of casualties.

Mustard appears to chemically injure in a number of ways. It does not directly and immediately destroy tissues like most of the other agents, rather, it chemically does its damage on the inside by reacting with key parts of cells. The mustard is absorbed into almost all tissues easily passing through cell walls. Once inside it can form a sulphonium ion that reacts with base compounds of the cells DNA (alkylation). This bonding then induces breaks in the DNA strands and the forming of bridges between the two strands of DNA. Most cells in the body must divide to reproduce and replace themselves and these bridges prevent the DNA from producing new cells. The old cells die out without producing replacements. This damage has also led to a number of higher incidences of cancer to those people exposed to mustard.

Another way it injures is direct reaction with and damage to intracellular glutathion. Glutathion is a small peptide molecule that removes free radicals from the cell during respiration when oxygen is taken in and the carbon dioxide is removed. These free radicals are very toxic and if enough mustard ties up all the glutathion, the cells are destroyed from the damage. This is how the blisters start on the skin. The cells are so damaged that they die out in a few hours and are not replaced.

Mustard can also bind to a large number of proteins, nucleophiles, and other biological molecules. At all these binding sites it effectively destroys the substance and the living cell around it by alkylation. Because it waits until it is absorbed into human cells to do its damage, and it is invisible while doing this, it causes great and lethal damage inside of many parts of the body before anyone knows it is there. That is what makes it so effective a weapon.

The mustard agent initially injures only the surface cells it comes in contact with. If enough is brought into contact with the skin, it will be absorbed into the blood stream and be carried throughout the body. It also is distributed throughout the body if inhaled although most of it remains inside of lung tissue cells. The dose needed to kill with mustard is about 50 times greater than the weakest nerve gas, but its ability to wound deeply and cause casualties that tie up enemy resources and troops are often more valuable to an enemy than obtaining kills. Dead men don't tie up troops, wounded and crying men do.

The skin injuries from mustard require much longer to heal than do thermal or other kinds of chemical burns. They often require long periods of recuperation and sometimes plastic surgery is necessary. Eye wounds that do not cause permanent blindness may cause light sensitivity, swollen eyelids, and cornea injuries that persist 30-40 years after the initial exposure. Most deaths result from complications associated with lung injuries caused by the mustard. Pulmonary edema and chemical pneumonia are the most common causes.

Mustard also damages the bone marrow, spleen, and lymphatic tissue which can reduce white blood cell count to near zero in 5-10 days after exposure which reduces the immune defense at a time when the body is experiencing many infections. This condition is similar to radiation poisoning.

There is no treatment or antidote for mustard, you can only treat the symptoms. Decontaminating the skin, removing clothes, washing thoroughly, shaving hair off the head if it may contain chemical agent, and using eye wash are the first things that must be done. Use of antibiotics and antiseptics to control infection, as well as local anesthetics for the pain is required. The lung injuries are treated with bronchodilatory methods. Medicine to relieve coughing and use of cortisone is helpful. Despite treatment, the injuries may remain for many years after exposure.

Mustard agents use special weapons designs to make them more effective. Since it freezes at 57 F, it is usually mixed into a solvent that lowers its freezing point. The Germans and French use 10-25% carbon tetrachloride, chlorobenzene, and nitrobenzene depending on the time of year. The U.S. used chlorpicrin as its solvent because it was also toxic. The solvents also had the effect of making the mustard more volatile, especially in winter where it mostly depended on contact with footwear. The gas was distributed by bursting charges in shells which scattered it into gas clouds, or some shells would distribute it as a finely divided spray as it passed overhead without exploding. The mist would resemble fine rain which would cling to clothing and vegetation. The gas clouds were invisible and were effective for up to 6 hours on open terrain and 12-24 hours in areas with vegetation to protect it from the wind and sun.

The droplets and gas penetrate targets with great speed and quickly contaminate all clothing and vehicle surfaces they touch. This liquid is then carried about into places that were uncontaminated and thought safe such as dugouts and areas far behind the lines. The wind blowing across the contaminated areas will carry vapor as much as 500-1,000 yards in lethal concentrations.

Because of its high toxicity, its ability to attack all tissues, its great persistence in the battle area, its lack of warning symptoms and invisibility, its ability to penetrate protective clothing, its easy ability to be manufactured almost anywhere, the wide availability of raw materials in all developed countries, its chemical stability, and its ability to withstand explosions, all make it one of the most potent weapons ever developed for war.

Chlorvinyldichlorarsine is called "Lewisite" by the Americans after its inventor Dr. W. Lee Lewis who first prepared it in 1917 for the American war effort. It is also known chemically as dichlorarsinoethane, dichloro [2-chlorovinyl] arsine, chlorovinylarsinedichloride, and Lewisite. It is a colorless liquid that may have a violet to brown appearance when impure. It has a geranium like odor which cannot be detected at the lower concentrations where it causes harm.

The Germans had developed the ultimate defense in mustard gas in 1917 but their offensive plans for fast acting non-persistent chemical agents had been considered a failure on the front. The use of Green Cross (Diphosgene), and Blue Cross (Diphenylchlorarsine) together had failed to produce any major breakthroughs. The American army closely watched the developments and realized that they would need an offensive chemical that would be fast acting, non-persistent so the troops could soon move into the area, and would act on the whole body like mustard gas. An intensive effort to produce an arsenical compound that fit the bill was begun and Lewisite was the result of that work. Their were however large technical problems that needed to be overcome in order to mass produce it and these were not solved until late 1918 when the first manufacture of it began. The first lot was finished in November when the armistice was signed and it was destroyed at sea without ever being used in the war.

It is soluble in most organic and petroleum solvents and is itself a solvent for mustard liquid and it is used this way in current U.S. and British stocks. It is chemically stable and is not dissolved by water or weak acids.

Like mustard gas, Lewisite is readily decomposed by alkalis like 5% solutions of caustic soda or ammonia and this process is sped up by heat (hot water). Also like mustard gas, Lewisite will readily penetrate clothing, leather, rubber, and all the tissues of the body making it as deadly a choice on the battlefield and as hard to protect against.

Its vapor pressure is much higher than that of mustard gas.

Temperature	Lewisite	Mustard
0 C	.087 mm Hg	.026 mm Hg
20 C	.395 mm	.065 mm

The volatility of Lewisite at 68 F (20 C) is 4.5 mg/ liter while mustard is .625 and because of this it is much less persistent on the battlefield. The persistency of Lewisite is 9.6 times that of water at 68 F, while mustard is 67 times that of water. Its freezing point is -18 C (0 F) so it does not require a solvent by itself for storage, and it is stable in storage and like mustard does not attack iron or steel.

Lewisite is a systemic poison and is easily absorbed through the skin. When applied topically, only 2.6 grams is required to kill a 150# man which is about the amount that will fit under a fingernail. [.0173 grams per pound of body weight]. Its minimum irritation concentration is .0008 mg/ liter which is far below its detectable level in air (by odor). Its blistering concentration is .334 mg/ liter which is 1/10th its saturation level in air which makes field concentrations 10 times this level possible on the battlefield. When inhaled, its fatal concentration in 10 minutes is .12 mg/ liter and at 30 minutes is .048 mg/ liter so its toxicity is slightly greater than that of mustard gas. It acts a systemic arsenic poison in low concentrations.

The main advantage of Lewisite over mustard is that it is faster acting on the troops. A few drops are completely absorbed in 5 minutes on the skin with a burning sensation (human government tests). It reddens at 10-30 minutes with erythema spreading rapidly. Blistering begins in about 13 hours with infection setting in at 24 hours. Military tests indicate it is superior to any of the WW1 gases including Mustard agent and it is incorporated into the chemical weapons stocks of most major powers today. The modern mixture is designated HL in the U.S. arsenal.

An antidote of sorts for the skin exposure was developed by the British called BAL for British Anti Lewisite which reduces injuries to the skin and mucous membranes. The chemical name for the antidote is "dimercaptopropanol".

Methyldichlorarsine [CAS# 593-89-5 CH_3AsCl_2] known as methyl dick in Germany and designated MD by the Americans, it is the methyl analogue (equivalent) to the ethyldichlorarsine described earlier with many of the same properties. It was intensely studied by the Americans toward the end of the war but was not actually used in combat. The Germans failed to use it because they considered its manufacture to be too complicated.

Dibromomethyl Sulfide is the bromine analogue of mustard gas and was called "Bromlost" by the Germans who were searching for a more persistent agent than mustard gas that would contaminate ground for long periods that would be yielded to the enemy. The elements that hydrolyze mustard once it is dispersed are humidity, temperature, and wind. A compound with lower vapor pressure, a higher boiling point, and less hydrolysis would be more effective than mustard. Although there were high hopes for this compound it did not meet expectations.

Bromlost is a solid which melts at 70 F (21 C) and boils with decomposition at 250 C (464F). Its volatility is .4 mg/ liter or about 50% greater than mustard, and its specific gravity is 2.05. It turned out to be more easily hydrolyzed than mustard. It also turned out to produce the same symptoms and effects as mustard but required greater doses to produce them. It is about 50% more dense than mustard which would allow more material to be loaded into the shell but its easy destruction from moisture made it less effective overall. It is made by the same as mustard using bromine chloride instead of sulfur chloride.

Systemic Toxic Agents

Hydrocyanic Acid [CAS# 74-90-8 HCN] also known as prussic acid, hydrogen cyanide, and formonitrile, is a water white liquid below its boiling point of 26.5 C. It has a faint odor of bitter almonds and freezes at -13.3 C. The French called it "Vincennite, Manganite, and Forestite" while the British designated it JL and VN. It is soluble in water, weakly acidic and sensitive to light. When not pure or stabilized , it can polymerize spontaneously with explosive violence. The stabilizer used in modern commercial production is .05% phosphoric acid.

HCN is made by

1. Reacting methane or natural gas with ammonia and air catalytically.
2. Recovery from coke oven gases.
3. Reacting bituminous coal and ammonia at 1250 C.
4 It occurs naturally in some plants such as almond and oleander.

For 100 years before WW1 hydrocyanic acid was well known as one of the most deadly poisons ever made. It had already been used in deliberate poisonings (and since by the former soviet union in many well publicized assassinations). The French became its only proponent during the war while all the other countries felt it was not suitable for use as a delivered gas weapon. At the end of 1915, the French had filled large quantities of gas shells with hydrocyanic acid called "special shells #4). At first they hesitated to use them because of their high toxicity and splinter effect. They had agreed to the Hague convention to not use gas shells that had poisonous materials with a toxicity greater than its splinter effect. Although events in the war effectively relegated the agreement to the history books, French leaders still took their agreements for the rules of war seriously in 1915.

In response to the German use of poison shells, the French lost their timidness and on Feb 21, 1916 they began to deliver phosgene shells and finally on July 1, 1916, in the battle of the Somme they fired "Vincennite" shells containing hydrocyanic acid. Although the German gas masks at this time provided adequate protection against phosgene, they were not designed to defend against HCN attacks. This was short lived however as the Germans quickly devised new filters for their canisters which contained 1 gram of pulverized silver oxide scattered throughout the potash layers and this was adequate to react with the HCN and protect the wearer.

During WW1 the French produced their HCN by mixing a solution of potassium or sodium cyanide with dilute sulfuric acid and distilling off the gas. The vapors were absorbed in water from which it was separated by fractional distillation. Its specific gravity is .7 and its vapor is only .93 times as heavy as air. It is very volatile (873 mg/ liter at 20 C) making it very deadly to work with. Because of its high volatility it can only persist in the target area a few minutes after which it dissipates and rises into the atmosphere.

In order to slow down its volatile nature, it was dissolved into stannic chloride with chloroform added as a stabilizer to prevent polymerization in the shells called "Vincennite". It was also dissolved in arsenic trichloride with weak acids added as stabilizer.

Hydrocyanic acid is a true blood gas or poison. It binds with substances in cells and tissues and prevents oxidation which results in asphyxiation. At the same time it attacks nerve cells and induces paralysis. When injected under the skin a dose of .05 gram is lethal and the LD50 by inhalation is even lower. The poisoning effect is not cumulative and up to about a dose of .03 mg/ liter the body can eliminate the HCN without long term ill effects. Above this dose the critical concentration is reached and death occurs very quickly.

The HCN was so volatile and its vapors being lighter than air, it became almost impossible to achieve lethal concentrations in air long enough to be effective. The artillery shells used by the French produced no known casualties despite using over 4,000 tons during the war and it illustrates the problems with using dangerous chemicals that are not suitable for delivery on world battlefields. HCN will have to remain in the realm of the professional poisoners rather than in the Generals warplans.

[In the authors opinion, the HCN could have been used as an excellent positioned defensive weapon by releasing its vapors at the desired rate into underground hoses of abandoned areas. More will be said about this in the final chapter on weapons design.]

Cyanogen Bromide [CAS# 506-68-3 BrC N] was first used in war by the Austrians in September 1916 and was called "CE". The British would also use it in artillery shells on the western front under the designation "CB". This second attempt to find a cyanide based poison gas that would be effective appeared promising. The cyanogen bromide exerts similar toxic effects on the body like hydrocyanic acid. Its dose overall is less toxic, being lethal at .4 mg/ liter in 10 minutes which is still more toxic than phosgene, and it is a strong irritant at .006 mg/ liter affecting the conjunctiva and mucous membranes of the respiratory tract. It is unbearable at .035 mg/ liter.

The cyanogen bromide is a white crystalline solid with a penetrating odor that melts at 52 C (126.4 F), and boils at 61.2 C (142 F) producing a vapor 3.6 times heavier than air. It is soluble in alcohol and water but cold water slowly decomposes it. It has a specific gravity of 2.02 and a vapor pressure of 92 mm Hg at 20 C (68 F). Its volatility is 200 mg/ liter making it one fourth as volatile as hydrocyanic acid and yet still be considered volatile with little persistence. This allowed for lethal concentrations to be achieved on the battlefield.

The original Austrian shells were loaded as mixtures of 25% CE, 25% Bromacetone, and 50% Benzene. The CE was extremely corrosive, attacking most metal surfaces which created many storage and handling problems, and it also polymerized and decomposed in storage which reduced the actual toxic effect when used in battle. The advantage of using it was so slight that the Austrians soon abandoned it in favor of the German Diphosgene (Green Cross) shells.

Cyanogen Bromide was made by directly reacting a solution of concentrated potassium cyanide with Bromine at 0 C in which the crystals precipitated. It is also made in modern industry by the combined interaction of sodium bromide, sodium cyanide, sodium chlorate, and sulfuric acid. It is used as a parasiticide, as a fumigant, rat extermination, and in gold extraction from mined ores.

Cyanogen Chloride [CAS 506-77-4 CNCl] was developed by the French after their failure with HCN in an attempt to use their stocks of cyanide in a heavier gas form that would be toxic in low concentrations. Cyanogen chloride is about as toxic as HCN and it is lethal at .4 mg/ liter. It kills by rapid paralysis of the respiratory system and nervous system and it is an irritant at .05-.1 mg/ liter. It also is a strong lacrimator at .0025 mg/ liter giving it several advantages over the HCN.

Cyanogen Chloride is a colorless gas or liquid that freezes at -6 C, and boils at 12.5 C producing a vapor 2.1 times as dense as air. It is soluble in organic solvents and water which slowly decomposes it in storage to cyanogen trichloride which is much less toxic. The first French shells were called "Mauguinite" and were marginally effective due to decomposition and high volatility (higher than HCN). The volatility in this form was 3,300 mg/ liter with a vapor pressure of 1,000mm at 68 F. They experimented and found that it was very stable when dissolved in arsenic trichloride which also increased the density of its vapors making it more lethal. They mixed both of these together in shells called "Vitrite" which were much more effective.

The Cyanogen Chloride was made by directly chlorinating Potassium Cyanide at 0 C. It is made in modern industry by suspending sodium cyanide in a solution of carbon tetrachloride which is kept cooled to -3 C and then chlorinated. It is used in low concentrations in some modern tear gas formulas and as a warning agent in fumigants.

Chapter 4

Military Phosphorus and Nerve Agent Weapons

"If there is one good reason to teach every living soul on the entire planet how to make nerve gas, it would be the mere existence of lawyers!"

Those military weapons built around the element phosphorus represent an entirely different class of ordnance that deserves its own place in the history of warfare. From the use of phosphorus to generate smoke, start incendiary fires, and severely burn personnel in modern napalm, to the unique application of simple chemicals that easily pass into the body and interfere with life functions in tiny amounts, phosphorus has changed the future of warfare almost to the same extent that nuclear weapons has.

Chemical History of Phosphorus for War

Phosphorus was first discovered and separated from other elements in a pure fashion in 1669 by a German chemist from Hamburg named Hennig. He distilled it as a vapor from urine and found that it glowed in the dark and burst into flame once he exposed it to the air. It was named phosphorus for "the mineral that produces light". Soon afterwards, many derivatives of phosphorus were also discovered such as phosphorus pentoxide, which, when it was dissolved in water would yield phosphoric acid.

In 1770, it became known that phosphorus was an essential component of animal bones and teeth and soon after its value as a fertilizer was recognized, resulting in the large scale use of animal bone meal to enhance crop yields. The next commercial use for phosphorus came in 1812 with the invention of striking matches which contained a mixture of sulfur, ground glass, glue, an oxidizer, and red phosphorus for the tip. Toy pistol caps would also soon be invented using potassium chlorate in one compartment and red phosphorus in another compartment. When brought together by striking, they would produce a small explosion. Finally, in 1842, chemists named Lawes and Murray would patent the mixing of sulfuric acid and ground bones to yield phosphoric acid directly. This would give rise to all the worlds fertilizer industries drastically increasing food production and allowing the support of the large urban populations in the world today.

In 1885, the invention of the electric furnace allowed for white phosphorus to be produced directly from ores by heating mined phosphate rock with coke and silica. This made it possible to generate large amounts of elemental phosphorus for the first time and would soon open up the discovery and invention of thousands of phosphorus based compounds.

In 1820, in separate research, scientists produced crude alkyl phosphates by reacting alcohols with phosphoric acid and this would eventually lead to the discovery of thousands of nerve acting phosphorus compounds more than century later in Germany. Throughout the 1800's, phosphorus was being discovered in almost every part of every living cell and soon the sciences of organophosphate chemistry was born. It would soon be known that phosphorus is used in every energy exchange reaction in the body, every transmission of nerve impulses, and in every part of our DNA, the code for all life. It was also learned that it could be used to harm life processes and would soon be used in this role as pesticides and nerve agents.

Basic Chemistry of Phosphorus

Phosphorus is not found free in nature and is almost always found in its fully oxidized form (phosphorus containing oxygen) called phosphates. These are widely distributed in the oceans, rock deposits, soil, in most foods, animals, all living cells, and in most man made materials in combination with nitrogen.

Phosphorus belongs to the chemical group called the "Pnictides" which include Nitrogen, Phosphorus, Arsenic, Antinomy, and Bismuth. Nitrogen and Phosphorus are found in all forms of life at about 3% and 1% respectively by weight. Phosphorus resembles arsenic in its chemical properties in which it reacts to fill its outside 3p orbital shell with three unpaired electrons In almost all of its compounds, phosphorus reacts to form 3, 4, or 5 covalent bonds with other atoms in which four are the most common and important.

The oxidation state or "oxidation number" is the number of electrons that can be added or subtracted from an atom in its combined state that will convert it back to its elemental form. Phosphorus compounds can exist in a number of oxidation states which are related to the number of attached oxygen atoms. Some examples along with their names and formulas are given here as examples. [R can be any element that fills its outside shell in the example given]

Phosphines	PH3	PR3	-3
Diphosphines	H2P-PH2	R2P-PR2	-2
Phosphine Oxide	R \\ R - P = O / R		-1
White Phosphorus	P4		0

```
                                 H   O          R     O
                                  \ //           \   /
Phosphinic Acid or                 P              P                +1
Hypophosphorus Acid               / \            / \
                                 H   OH         R   OR

                                   OH   OH
                                   |    |
Hypodiphosphoric acid          H - P  - P - H                      +2
                                   |    |
                                   O    O


Phosphorus Acid                 OH              OH          OR
Phosphonic Acid                /               /           /
Phosphite Esters           H - P - OH      R - P - OH    P - OR          +3
                               \\              \\          \
                                O               O           OR

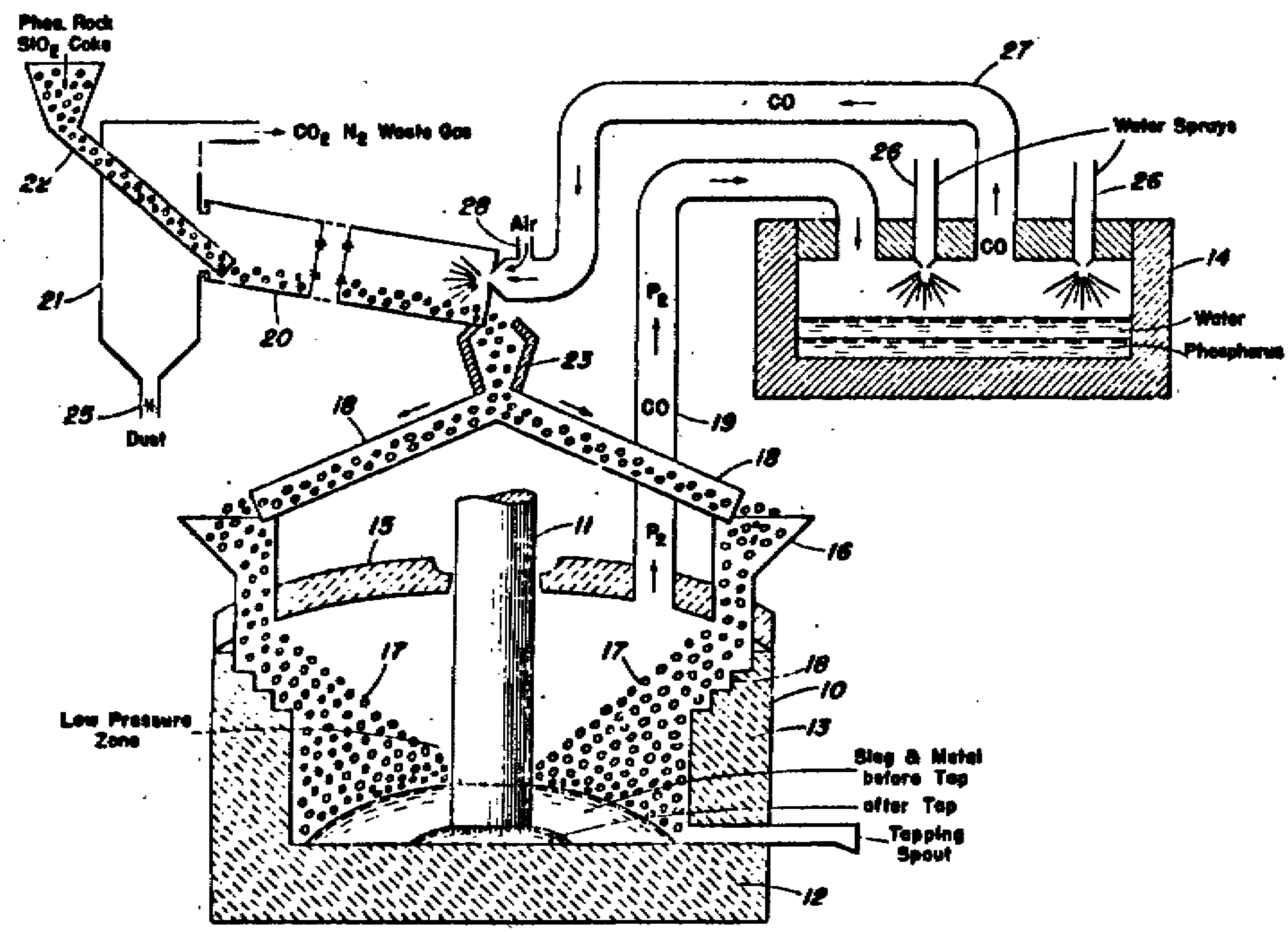

                                HO      OH
                                  \    /
Hypophosphoric Acid             O = P - P = O                            +4
                                   /    \
                                 HO      OH


                          HO   O          RO   O
Phosphoric Acid             \ //            \ //
Phosphoric Esters            P               P                           +5
                            / \             / \
                          HO   OH         RO   OR
```

Phosphorus exists in nature almost exclusively in the +5 oxidation state. Phosphine (PH3) -3 oxidation state is absent from all biochemical and geochemical systems on earth. Phosphorus has a very strong affinity for oxygen and prefers it forming strong bonds that prevents its easy reaction with many other materials in preference for the oxygen. This is why the many alcohols and halogens that form the thousands of nerve acting phosphorus compounds were not discovered until only recently in chemical history. The phosphorus could not directly react with the alcohol parts to form nerve agents in most of its normal physical states. It needs to be prepared in special chemical forms in order to make it reactive enough to form the nerve agent molecules.

White Phosphorus (WP)

Elemental phosphorus (white, red, and black) was the first of the phosphate materials to be used in a large scale in war. It is produced in an electric furnace in large volume by heating phosphate rock or phosphoric acid with a carbon source like coke or coal with silica (sand). The phosphate rock is usually introduced with silica and coke into a rotary kiln that heats it to 500-600 C (diagram from patent #2,820,396 illustrates the idea) which begins to fuse the materials. They are sintered at 1200-1300 C and then fed into an electric furnace that employs electrodes that arc across the minerals heating them into a molten mass at 1400 C by which time the fluorine in the mix has reacted with the silica and passed out as a gas (SiF4) and the carbon reacts with the oxygen in the phosphorus to form carbon monoxide which also comes off as a gas. At about 1550 C, the elemental phosphorus finally distills off as a vapor and is distilled off in the CO atmosphere (no oxygen) where it condenses back into a liquid and solid under water as shown.



Approximately 2000# of phosphate rock is mixed with 700# of silica and 400# of coke to effect the above reaction. It proceeds as -

$$2\ Ca_3(PO_4)_2 + 5C + 3SiO_2 = P_4 + 5\ CO + 3\ CaO\ SiO_2 \text{ and/or } SiF_4$$

The fluorine can also be driven off without it reacting with silica as HF.

Phosphoric acid can be heated in the same manner directly to produce the phosphorus simply by adding coke (or charcoal) alone to the acid and heating above 1600 C.

$$4\ H_3PO_4 + 10\ C = 4\ P + 10\ CO + 6\ H_2O$$

The furnace usually contains two electrodes that produce an arc that generates heat inside the molten mass of more than 2000 C in many modern furnaces.

The white phosphorus produced is a soft, white waxy solid of 1.8 specific gravity which melts at 44 C (111 F) and boils at 287 C (549 F). In this form it is one of the most reactive substances known and it combines with the oxygen in the open air so vigorously that it bursts into flames quickly with a fire that can only be put out by immersing completely under water. For this reason it is usually stored under water, alcohol, or is dissolved in carbon disulfide, fats, or gasoline/benzene for use in incendiary weapons such as gasoline thickened by styrene (napalm).

The napalm containing phosphorus produces burns in human tissue that were terribly painful and slow and difficult to heal. This made it an effective psychological weapon which improved its tactical effectiveness in war. As an incendiary, it would only ignite easily combustible materials and was less effective in this role than thermites and jelled gasoline. Phosphorus has also been used to generate large volumes of smoke for cover and was more efficient at generating massive smoke clouds than oil and other materials. It was difficult to store and handle, produced bright flames when ignited in air, and in its solid form could not be sprayed without first dissolving in highly flammable and dangerous solvents. This has led to its replacement in this area by more suitable materials.

Factory workers in white phosphorus plants who were exposed to small amounts of the fumes developed a condition known as "phossy jaw" that was a 100% fatal necrosis of the jaw tissues. For this reason its use in matches was banned and improvements in safety were quickly adopted in plant operations. White phosphorus itself is a powerful poison and as little as 50 mg is usually fatal.

In ordinary production, the phosphorus is often "burnt" by exposing it to air or carbon dioxide which causes it to burst into flames and oxidize into a material called phosphorus pentoxide (P_2O_5 or P_4O_{10}). The reaction is -

$$P_4 + 5\,O_2 = P_4O_{10}$$
$$P_4 + 10\,CO_2 = P_4O_{10} + 10\,CO$$

The first reaction is the one that generates smoke and has been used in military smoke generators. White phosphorus is virtually insoluble in water and is easily stored, fused, and transported safely under an aqueous layer.

The phosphorus pentoxide is condensed in a cooling chamber after it is burnt into the familiar white powder used commercially. It melts at 423 C and combines quickly with water to form orthophosphoric acid (H_3PO_4). One of its important reactions is to heat it with diethyl ether in an ethylene atmosphere at 180 C to yield triethyl phosphate which is used in many nerve acting chemicals. The reaction proceeds as -

$$P_4O_{10} + 6\,Et_2O \text{ in } C_2H_4 = 4\,(EtO)_3PO$$

It can also be used to prepare phosphorus oxychlorides (next section) and dehydrate acids. It will also allow the production of elemental phosphorus by heating with carbon -

$$P_4O_{10} + 10\,C = 10\,CO + P_4$$

Black Phosphorus is formed by placing white or red phosphorus under high pressure. It can also be made by heating white phosphorus in the presence of mercury with a black seed crystal. Black phosphorus is the least reactive of the phosphorus element and is hard to ignite although impact can often cause it to burst into flame. It is electrically conducting, it physically resembles graphite and is insoluble in most solvents.

Red Phosphorus represents a variety of different forms that resemble black phosphorus, is almost non-toxic and has replaced white phosphorus in match compositions. Powdered red phosphorus can explode when ignited in air and is made by heating white phosphorus at 260 C for 48 hours, or amorphous black at 125 C, or its crystalline form at 550 C. It will combine directly with oxygen, sulfur, halogens, and metals although they are generally less vigorous, and it does not react at all with alkali unlike white phosphorus which yields deadly phosphine gas when exposed to and reacted with alkali. Exposure to damp air causes red phosphorus to slowly oxidize to orthophosphoric acid. It can be used to safely react with sulfuric acid to yield the elemental sulfur as -

$$4\,P + 8\,H_2SO_4 = 4\,H_3PO_4 + S + 7\,SO_2 + 2\,H_2O$$

Phosphine (PH_3) is a very poisonous, colorless gas with an unpleasant garlic like odor that is produced by the reaction of water or dilute acids on metal phosphides (see volume 4-Incendiaries), by reacting caustic potash with phosphorus or phosphonium iodide, or by heating dry phosphorus acid [H_3PO_3 + Heat = $3\,H_3PO_4$ = PH_3]

It can also be made by directly reacting ammonia with phosphorus vapors.

$$2P + 2 NH_3 = 2 PH_3 + N_2$$

It is spontaneously flammable in air and acts like arsine in poisoning the bodys tissues very quickly. The unique aspect of this gas is that it forms phosphates once the target individual is dead making it impossible for the coroner to chemically determine the cause of death when this gas is involved unless their is other uninhaled evidence of its presence. This makes it a favorite of professional assassins. After an exposure of about 1 part in 4,000 for an hour the poisoning takes about 1-2 days before the symptoms are observed. The target has difficulty breathing with chest pain. The remaining symptoms resemble arsenic poisoning and their is no antidote or effective treatment. Because it changes its chemical composition in the body, it becomes impossible to detect making it a sneaky weapon and a good substitute for more dangerous gas weapons. 125 grams of phosphorus is required to produce 3/4 of a cubic foot of pure phosphine vapor at normal density.

Phosphorus Chloride Chemistry

In order to make phosphorus reactive enough to combine with the various other compounds that make up nerve agents like the different alcohols (or alkane equivalents) it is usually necessary to form chemical compounds with a halogen such as chlorine or fluorine on either the phosphate or the alcohol. The phosphate and alcohol will not ordinarily react with each other in the desired order or combinations. If you mix phosphoric acid and an alcohol they will barely react at all (after boiling together for 24 hours) because of the strength of the P-O bonds. By preparing an alcohol with chlorine as part of its molecule, or by attaching a halogen like chlorine to the phosphorus in a number of possible ways, a special reactive material is made that can now be brought together to form the organophosphates.

The main phosphorus chlorides used to prepare the toxic organophosphates we know as nerve agents and pesticides are Phosphorus Trichloride, Phosphorus Pentachloride, and Phosphorus Oxychloride. The US government bans the sale of these phosphorus chlorides to all countries considered to be a terrorist threat to the free world and a number of people have been arrested and imprisoned in the US for attempting to sell these materials overseas.

Phosphorus Trichloride can be produced by reacting elemental white phosphorus with sulfur chloride or thionyl chloride as follows -

$$P_4 + 6 S Cl = 4 PCl_3 + 12 S$$

and

$$P_4 + 8 SO Cl_2 = 4 PCl_3 + 4 SO_2 + 2 SCl$$

The first reaction can also use sulfuric acid as a substitute to yield elemental sulfur and phosphorus pentoxide. This can be of great advantage to recover elemental sulfur from battery acid and other sulfuric acid sources when governments restrict the supply of sulfur to its populations. Elemental sulfur is important in many explosives (Vol 3) and in the manufacture of mustard gas (last chapter).

Other chemical methods of producing PCl3 include reacting phosphorus oxychloride over red hot coke -

$$POCl_3 + C = PCl_3 + CO$$

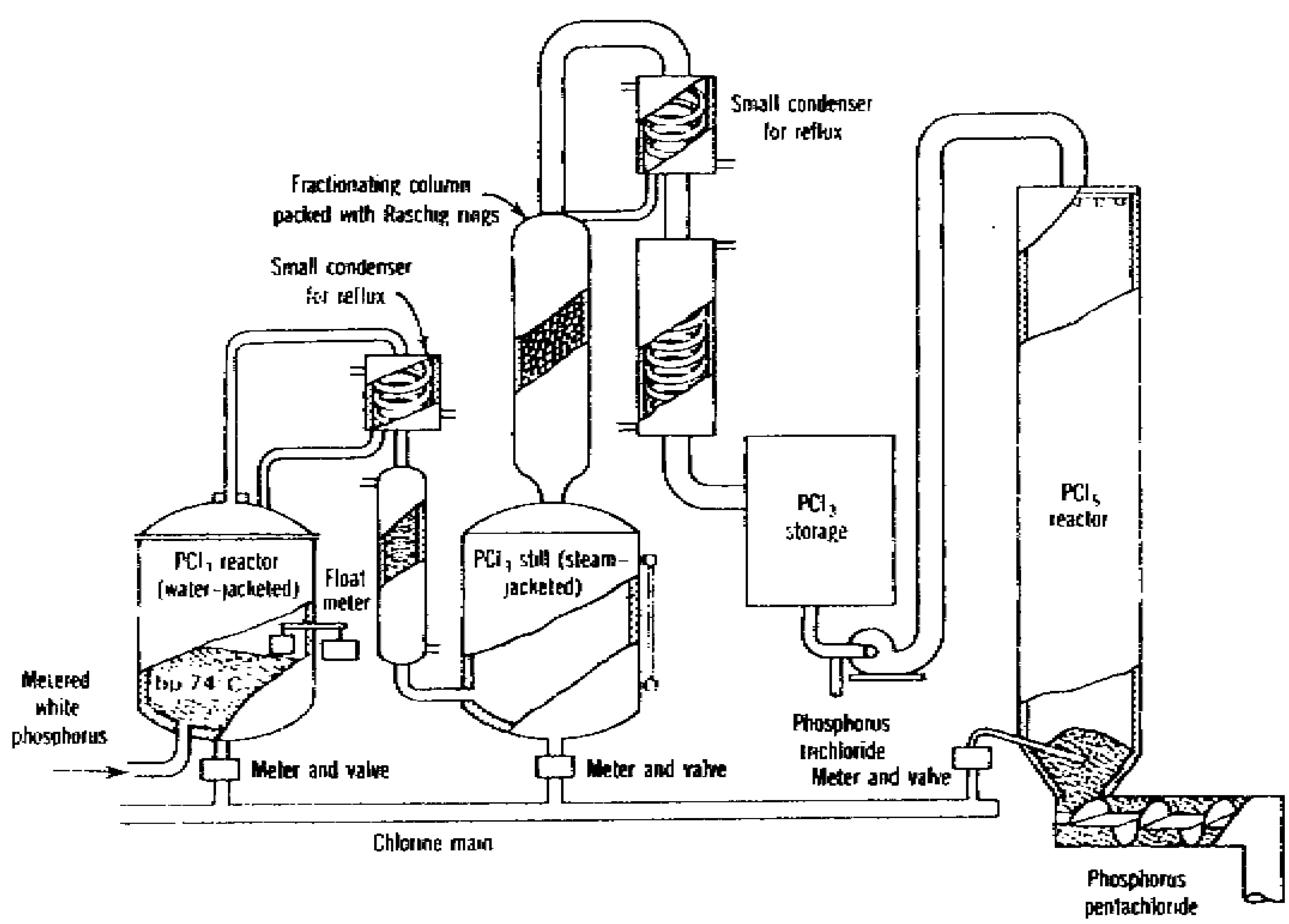
Reacting with various halides like $HgCl_2$, $CuCl_2$, or SO_2Cl_2 -

$$2P + 3SO_2Cl_2 = 2PCl_3 + 3SO_2$$

or by reacting phosphorus trioxide directly with hydrochloric acid

$$P_4O_6 + 6HCl = 2H_3PO_3 + 2PCl_3$$

The phosphorus trichloride can also be produced commercially by the direct action of chlorine gas on red phosphorus suspended in seed PCl3 while white phosphorus will give a purer industrial product. The diagram below illustrates the plant manufacture of PCl3 which is refluxed continuously to provide seed material. The plant can also simultaneously produce phosphorus pentachloride.



Chemically, the phosphorus trichloride has a lone pair of electrons in its outer 3s shell and it has a highly polar nature of its P-Cl linkage which means that it will react with an enormous number of other chemicals to yield a variety of different phosphorus compounds. A few examples include - [Note - When the letter R is used in a formula, it does not represent a single element. It is intended to represent an alcohol or its alkane equivalent which will be described in more detail in the section on organic chemicals shortly.]

PCl3	+	BBr3	=	Cl3PBBr3
		As2O3		P2O5
		AlCl3 + CH3Cl		CH3PCl3 AlCl4
		O2, SO2, ClO2		POCl3
		S		PSCl3
		H2O		H3PO3
		Cl2		PCl5
		AsF3, ZnF2		PF3
		Sb		P
		HI		PI3
		PBr3		PCl2Br + PBrCl2
		S2 Cl2		PCl5
		NH3		P(NH2)3
		RCOOH		RCOCl
		AgCN		P(CN)3
		AgNCO		P(NCO)3
		RMgBr		R3P

PCl3	+	ROH	=	(RO)3 P
		RSH		(RS)3 P
		RP(OR)2		RPCl2
		R2POR		R2PCl
		R2NH		(R2N)3 P
		N2O4		Cl3P NPOCl2
		Ni(CO)4		Ni(PCl3)4
		2 CrO3		POCl3
		ClO2		POCl3
		SO3		POCl3
		AsH3		AsP

The above reactions which yield phosphoryl chloride (phosphorus oxychloride-see next section) is especially important because both of these phosphorus chlorides are widely used in the manufacture of the organophosphite esters and ultimately in the wide range of nerve acting organophosphates. Simply adding a small amount of oxygen (from the air) will oxidize the phosphorus to POCl3 also.

Phosphorus Oxychloride (also known as phosphoryl chloride) can be prepared from the reaction of phosphorus pentoxide and hydrochloric acid or phosphorus pentachloride as follows

$$P_4O_{10} + 3\,HCl = POCl_3$$
$$P_4O_{10} + 6\,PCl_5 = 10\,POCl_3$$

It can also be made by heating the pentoxide with rock salt -

$$P_4O_{10} + 6\,NaCl = 2\,POCl_3 + 2\,Na_3PO_4$$

Other commercial routes of manufacture include heating Phosphorus pentachloride (PCl_5- next section) with oxalic acid or boric acid. The oxychloride is stable above 300 C, it yields phosphoric acid on hydrolysis (water added) and is used widely in the manufacture of nerve acting phosphate esters. The main source of oxychloride is from the pentachloride, but it can also be made by careful oxidation from air, oxygen, or other oxidizing agents like potassium chlorate as well.

```
Cl        O
  \      //
     P              =        POCl3
   /  \
Cl     Cl
```

The following reactions include boric acid, alcohols (R), oxides of nitrogen, sulfur, oxalic acid, calcium phosphate with chlorine and carbon monoxide, and iron phosphate and phosgene.

As you can see from the following reactions, there are many ways to produce the important phosphorus oxychloride. It can also be produced from many different starting materials so you are not limited to having to have an electric furnace to produce the important intermediates for nerve agent production.

Phosphorus oxychloride is a colorless fuming liquid that can also be made by many other routes. The following are a few examples.

PCl_3 +	$3HClO_3$	=	$POCl_3$	+	$3KCl$
PCl_5	$2H_3BO_3$		$3\,POCl_3$		$B_2O_3 + 6\,HCl$
PCl_5	ROH		$POCl_3$		$RCl + HCl$
PCl_5	N_2O_5		$POCl_3$		$2\,NO_2Cl$
PCl_5	SO_2		$POCl_3$		$SOCl_2$
PCl_5	$(COOH)_2$		$POCl_3$		$2HCl + CO + CO_2$
$FePO_4$	$3COCl_2$		$POCl_3$		$3CO_2 + FeCl_3$
$Ca_3(PO_4)_2$	$6CO + 6Cl_2$	+350 C =	$2POCl_3$		$3CaCl_2 + 6CO_2$

The last reaction is especially important because it allows the production of POCl3 without the use of furnace acid from feed diacalcium and tricalcium phosphates as well as the fertilizer calcium phosphates (triple superphosphate). Once POCl3 is produced, it is possible to produce all the nerve agents. The production can be accomplished simply by heating the materials together in an air compressor tank which may then be used for further reactions.

Phosphorus Pentachloride (P Cl5) can exist as P Cl5 in its vapor form but it forms a combination of P Cl4 and P Cl6 in its solid state-

```
   Cl  Cl               Cl   Cl       Cl  Cl   Cl
    \  /                 \   /+         \ |  /
Cl - P  - Cl              P               P
     |                   / \             / | \
     Cl                 Cl  Cl         Cl Cl Cl
```

It is a pale greenish solid with a pungent odor and is made by burning phosphorus in an excess of chlorine. Its reaction with water is violent. It is used as a chlorinating agent and as a catalyst as well as intermediate in many nerve agent reactions.

P Cl5 can also be made by bromine displacement - 2PBr5 + 5 Cl = 2 PCl5 + 5Br2
or by simple addition of chlorine by- PCl3 + S2Cl2 = PCl5 + 2PSCl3

The pentachloride can also be used in a wide variety of reactions some of which are -

PCl5 +	H2	=	PCl3
	H2O		POCl3
	I		+PCl4 ICl2-
	AsF3		+PCl4 PF6-
	P4S10		PSCl3 (This allows thiophosphates)
	KF		KPF6
	NH4Cl		(PNCl2)n (This allows phosphoroamidates)
	(NH4)2 SO4		Cl3P = NPOCl2
	P4 O10		POCl3
	BCl3		+PCl4 BCl4-
	R2 POOH		R2 POCl
	RP (O) (OH)2		RPOCl2
	PH3PO		PH3P+ - O - PCl5-
	H2N.NH2		Cl3P = N - N = PCl3 (allows diphosphates)
	PhNH2		Cl3P = NPh
	NH3		P+(NH2)4 Cl-
	CH3 COOH		POCl3
	SO2		POCl3
	R.SO2 OH		POCl3

As you can see from the above charts, once you have any of the chlorinated phosphates, you can easily make any of the others by a variety of routes.

Oxyhalides - POCl3 is an oxyhalide. Any of this group of phosphorus halides (POX3) can be used to produce toxic nerve agents.

```
F     O          Cl     O          Br     O
 \   //            \   //            \   //
F - P             Cl - P             Br - P
 /                 /                  /
F                 Cl                 Br
```

You can also have mixed species such as POF2Cl, POFCl2, POBr2Cl, etc. Phosphoryl Fluoride (POF3) is a very poisonous gas in its own right although it does not act as a nerve agent. It can be prepared by reacting a fluoride salt with the oxychloride. It is also used in the preparation of binary nerve agent weapons that will be described later.

Examples include Zinc, lead, sodium, or silver fluoride. Potassium fluoride dissolved in liquid sulphur dioxide will also work. The phophoryl fluoride is also obtainable by hydrolysis of PF5.

[Authors Note- There is one other important aspect of phosphorus chemistry that I would like to add here. When the raw rock phosphate is mined from the ground, it contains a small amount of uranium. This uranium can be separated from the rock after it is dissolved in sulfuric acid by using various solvents which precipitate it as a yellow cake. The demands for the yellow cake by the US nuclear weapons industry from 1950 to the end of the cold war in the 1980's was so great that large volumes of the processed phosphate in the US was solvent extracted to recover substantial amounts of uranium. It is interesting that both the nerve agent and nuclear weapons raw materials supplies were derived from the same basic sources.]

At this point, it is necessary to provide some information about organic chemicals. These organic materials are reacted with the phosphorus materials we have already described to form both intermediates and final end product nerve agents. It is important to understand what the names of these materials mean.

Toxic Organophosphates - Nerve Agents

The toxic organophosphates are chemically known as "phosphate esters", in which alcohols or their alkane equivalents are reacted with and attached to the element phosphorus. This process is called the esterification of phosphoric acids and alcohols. The first esterification took place in 1820 and in 1903 and 1915, substantial scientific papers describing the first synthesis of compounds containing phosphorus and nitrogen were published. These compounds were called amidates of phosphinic, phosphoric, and phosphorothionic acids. These amidates were the forerunners of the cholinesterase inhibitors that we know today as nerve agents. The first esters of pyrophosphoric acid were made in 1914 and in 1932 the first esters of phosphorofluoridates were discovered.

The earlier studies produced no observations of the poisonous properties of these materials until the mid 1930's when scientists in both Germany and England realized that they were potential chemical warfare agents and began extensive studies of them. The British scientist B. C. Saunders directed British research efforts centered mainly around the phosphorofluoridates and in 1941 first isolated and tested the compound DFP (diisopropyl phosphorofluoridate) on animals and on people including themselves. The properties that attracted the most attention were the very high toxicity and the miotic effects (contraction of the pupil of the eyes). The idea of using these substances as mists and aerosols which could kill at doses lower than 1 ppm led to this group of phosphates being called nerve agents. Two separate groups also in 1941 in England (Cambridge) would be the first to identify the biological cause of the poisoning to be the action of inhibiting cholinesterase and would describe their observations.

A German group at I.G. Farben in 1934, headed by Gerhard Shrader began to investigate the toxic organophosphates and in 1937 secretly patented the first one (without understanding the biological mechanism of the toxicity). They were primarily interested in the insecticidal properties of the compounds and by the end of WW2 they had produced over 2,000 toxic organophosphates in their labs including many of the insecticides and herbicides still in use today.
They discovered Dimefox in 1940, Schraden in 1942, and Parathion in 1944. By incorporating fluorine and cyanide into their compounds they discovered three extremely toxic compounds and promptly reported them to the German military. These were Sarin, Soman, and Tabun. They would soon discover hundreds of analogs to these compounds as well. Tabun was put into mass production near the end of the war and it is reported that as much as 12,000 tons had been stockpiled at wars end. Two Sarin plant were also being built but were never brought into actual production. This may have been due to the severely corrosive nature of Sarin which required silver contact surfaces for plant processing equipment and shell lining and which was in short supply at wars end.

After the war German research teams were divided up and headed organophosphate research for the US at the Army Chemical Center in Maryland, at Porton Wilshire in England, and at Suffield, Alberta in Canada. By 1950, the German scientist Schraden had discovered how to "activate" the phosphorothionates and phosphoroamidates which converted them from weak cholinesterase inhibitors to very potent nerve agents. The work was soon taken over from the German workers by scientists in the host countries as their expertise accumulated.

In the late 1950's, the Soviet Union released an enormous volume of technical information on the organophosphates. Speculation on their motives included the hope that other nations would develop them and directly confront the US without the Soviets having to engage in direct warfare. The building of the large nerve gas factory at Muscle Shoals, Arkansas in 1953 to supply the U.S. Arsenals at Denver Colorado, and Edgewood, Maryland probably had more to do with their decision to show off their know how.

One of the interesting historical footnotes came from captured documents in WW2. Adolf Hitler had wanted to use stockpiles of Tabun during the Soviet seige at Stalingrad. He was talked out of it by Schrader who told him that the technology for nerve gas was developed from american patents and they almost certainly had it as well, even though they never published it. Its use at Stalingrad would have almost certainly destroyed the Soviet armies but the British and Americans who were bombing Berlin would be able to depopulate the city in a single raid. In fact, the British had developed DFP but did not mass produce it. The United States had enormous stockpiles of nitrogen mustard and would have likely used it in retaliation of German first use against the Soviets with devestating effect.

In order to learn the science nerve agents it is necessary to learn the language of this type of chemistry. It is important to know and understand what the names of these chemical terms actually mean so I will describe the terminology that I will use in my book. Most of these terms are used by scientists in many countries but some may mean different things in different trade journals so that is why I am defining what they actually mean in this section of my book.

Organophosphates: is loosely used to describe all compounds which contain carbon and are ultimately derived from phosphoric and related acids.

The organophosphates are organized into groups according to their structure. In this structure will be the letters X, Y, and Z which can represent a wide array of compounds. For the toxic nerve agents, most of the X,Y,Z components are derived from short chain, unbranched alcohols.

Phosphate

```
X - O    O
    \  //
     P
    / \
Y - O   O - Z
```

Phosphonate

```
  X      O
    \  //
     P
    / \
Y - O   O - Z
```

Phosphorothionate

```
X - O    S
     \  //
      P
     / \
Y - O   O - Z
```

Phosphorothiolate

```
X - O    O
     \  //
      P
     / \
Y - O   S - Z
```

Phosphorodithioate

```
X - O    S
     \  //
      P
     / \
Y - O   S - Z
```

Phosphoroamidate

```
X
 \
X - N    O
     \  //
      P
     / \
Y - O   O - Z
```

Phosphorodiamidate

```
X
 \
X - N    O
     \  //
      P
     / \
X - N   O - Z
  /
 X
```

Phosphorofluoridate

```
X - O    O
     \  //
      P
     / \
Y - O   F
```

Phosphorochloridate

```
X - O    O
     \  //
      P
     / \
Y - O   Cl
```

Phosphonofluoridate

```
X      O
  \  //
   P
  / \
Y - O   F
```

Phosphoroamidothioate

```
X - O     O
    \   //
     P
    /  \
Y - N   S - Z
```

Chlorothionophosphate

```
X - O     S
    \   //
     P
    /  \
Y - O   Cl
```

Phosphonochlorothionate

```
X - O    S
    \  //
     P
    / \
   Y   Cl
```

Phosphonoamidothioate

```
   X     O
    \   //
     P
    /  \
Y - S   N - Z
          \
           Z
```

Phosphonium

```
X     Y
  \  /
   P
  /  \
Z     H
```

Phosphonothioate

```
X - O    S
    \  //
     P
    / \
   Y   Z
```

Phosphorodiamidic Fluoride

```
X
 \
X - N    O
    \  //
     P
    / \
X - N   F
 /
X
```

Phosphinofluoridate

```
X - N     O
   / \  //
  X    P
      / \
     N   F
    / \
   X   X
```

Phosphonoamidate

```
X - O     O
    \   //
      P
    /   \
X - N     Z
  /
Z
```

Phosphonic Diamide

```
X - N     O
  / \   //
 X    P
     / \
 X - N   N - X
   /       \
  X         X
```

Phosphorotrithioate

```
X - S     O
    \   //
      P
    /   \
Y - S   S - Z
```

When the chemical symbol is being described in long descriptive form, X, Y, and Z, are included in with the atom they are attached to at the start of each formula name. For example -

```
(CH3)2 - N      O
          \   //
            P
          /   \
  C2H5 - O     O - C3H7
```

This is called N,N-Dimethyl O-ethyl O-n-propyl, phosphoroamidate

What this means is that the first atom is N (nitrogen) and it is attached to Di (two) methyl groups. The next atom is the bottom left oxygen attached to an ethyl group and the lower right is an oxygen bound to an n-propyl group. The final name of phosphoroamidate describes the overall arrangement of the phosphorus atom attached to a double bonded oxygen, two single bonded oxygen's, and a single bonded nitrogen.

In some textbooks, the letters represent different compounds. In the below examples, the letter R represents an alcohol or alkyl group, the letter R' represents a separate alkyl group, and the letter X represents a -

1. Halide like fluorine or chlorine or bromine
2. an Alkoxy group (O - alcohol)
3. an Aryloxy group (O - aromatic hydrocarbon)

```
Phosphate    R - O    O          Phosphonate    R - O    O
                  \  //                             \  //
                   P                                 P
                  /  \                              /  \
             R - O    X                           R'    X
```

The possible variations of X are limited only to the imagination and the possible permutations of toxic organophosphates resulting from these combinations numbers in the tens of millions (more than all the currently known chemicals put together). Most of the most toxic organophosphates fall into the phosphate, any of the sulfur (phosphorothionic) bonded, and phosphonic categories.

When compounds are being described in short form, the letter designating the attachment is left off - for example, the compound below can simply be called

Dimethyl Ethyl Phosphonate

```
CH3 - O       O
        \   //
          P
        /   \
CH3 - O       C2 H5
```

If the X, Y, or Z is bound to a hydrogen (O - H), the term hydrogen may be used in the name -

Dimethyl Hydrogen Phosphate

```
CH3 - O       O
        \   //
          P
        /   \
CH3 - O       O - H
```

Some of the trade journals use the collective term "thioate" in place of the thiolate and thionate used to describe the sulfur bound phosphorus groups. Both descriptive methods will be used in this book.

Many toxic phosphorus compounds contain more than one phosphorus atom. These will be covered in a later section of this chapter.

In the pages that follow, we will describe each of the phosphorus groups in detail and give examples of how each are made. Most of these will be ordinary pesticides which are also usually toxic to people. After these basic concepts are learned, it is then possible to teach how the deadly forms of these can be made through isomerization and substitution.

Phosphates

are characterized by the central phosphorus atom attached to three single bonded oxygen atoms each of which forms another bond to an X, Y, and Z, and the final double bonded oxygen -

Phosphate

```
X - O     O
     \   //
       P
      / \
Y - O     O - Z
```

Chlorfenvinphos

```
C2H5 - O      O
        \    //
          P
         / \
C2H5 - O     O - C = CHCl
                   \
                    2,4-dichlorophenyl
```

This compound is an insecticide that is also known by the trade names SD-7859 (Shell), Birlane (Shell), and Sapecron (Ciba-Geigy). It is produced by -

1. Adding 2,4 Dichloracetophenone to triethyl phosphate over a period of 1/2 hour.
2. While adding the dichloracetophenone, maintain the temperature at 10-30 C by cooling as required.
3. This reaction mixture is then stripped by heating in a steam bath under 2 mm mercury pressure leaving a crude clear amber liquid that is the end product.
4. This liquid is then molecularly distilled at 6 x 10(-5) mm of mercury.

The above procedure originates from US patent # 3,116,201 - December 1963 and assigned to Shell Oil Co.

Dichlorvos (DDVP)

```
CH3 - O      O
         \  //
           P
         /  \
CH3 - O      O - CH=CCl2
```

is a contact and stomach insecticide with the chemical name 2,2-dichloroethenyl dimethyl phosphate. It is also known by the trade names Nogos and Nuvan (Ciba-Geigy), 19149 and Dedevap (Bayer), Vapona (Shell), Mafu, Oko, and Nerkol. It is produced by -

1. reacting trimethyl phosphate and chloral to yield the following reaction -
   (CH3O)3 P + Cl3 CCHO = (CH3O)2 P OOCH=CCl2 + CH3Cl

2. The range of the reactants mixed together can be 2:1 or 1:2. The reaction is exothermic. The temperature range used is 10-150 C and the reaction is concluded by heating at 50-150 C over 10 minutes to 1-2 hours.

3. A solvent such as benzene, toluene, or ether may be used (added) to control the heat during the reaction. A jacketed kettle that stirs the product mixture is suitable. The materials can be separated by distillation or solvent extraction.

This process is described in US patent #2,861,912 assigned to Ciba Ltd in November 1958

Dichrotophos

```
CH3 - O      O
         \  //
           P
         /  \
CH3 - O      O - C = CH - C - N (CH3)2
                 /          \
               CH3           O
```

is a systemic insecticide and acaricide which is chemically called 3-(dimethylamino)-1-methyl-3oxo-1-propenal dimethyl phosphate. It is known by the trade names SD-3562 and Bidrin (Shell), and C-709, Carbicron, and Ektafos (Ciba-Geigy).

It is produced as follows -

1. Mix 770 grams of 2-chloro-N,N-dimethylacetoacetamide with 100 ml of glacial acetic acid at 90-95 C.

2. Add 656 grams of trimethyl phosphate while constantly stirring for 1.25 hours while maintaining the temperature at 100 C while stirring and for 2.75 more hours.

3. The mixture is then stripped at a temperature of 110 C at 1.8 mm of mercury pressure.

4. App 1,044 grams of product is obtained which yields about 82% of the desired phosphate. Leaving out the acetic acid will yield a 50% product.

This and other procedures are described in US patents 3,068,268 of Dec. 1962 assigned to Shell oil and 2,802,855 of Aug. 1957 assigned to Shell Development Co.

Diethyl Methylprazolyl Phosphate

```
C2H5 - O      O
         \   //
           P
         /  \
C2H5 - O     O - methyl pyrazolyl
```

is an insecticide called O,O-diethyl O-(3-methyl-5 pyrazolyl) phosphate. It has been marketed under the names G-24,483 and Pyrazoxon (Ciba-Geigy AG). It is made by -

1. Sodium carbonate solution (280 parts of 2N) is neutralized by 49 parts of 3-methylpyrazolone-5, and the solution is evaporated to dryness.

2. This thoroughly dried salt is added to 500 parts of pure benzene and then 95 parts of diethyl phosphoric hydrogen (acid) chloride is added while stirring and this reaction mix is heated to 100-110 C for several hours. Sodium chloride salt forms which is filtered off.

3. The solvent may be distilled off but the end mixed product cannot be distilled without decomposition. It is ready to use as is.

This process is described in US patent 2,754,244 of July 1956 and assigned to J.R. Geigy

1,3-Di-(Methoxycarbonyl)-1-Propen-2-YL Dimethyl Phosphate

```
CH3 - O        O
        \    //
          P
        /    \
CH3 - O      O - C = CHCOOCH3
                    \
                     CH2 COOCH3
```

is a contact insecticide and acaricide, chemical name of Dimethyl 3-[(dimethoxyphosphinyl)oxy] -2-pentendioate, and known as GC-307 and Bomyl (Allied Chemical Corp). It is made by -

1. Dissolving sodium metal in alcohol to form an intermediate by adding dialkyl acetone dicarboxylate.

2. This reaction intermediate is then reacted with dialkyl chlorophosphonate to produce the final vinyl ester phosphate.

This and other methods are described in US patent 2,891,887 assigned to Allied Chemical Corp. in June 1959.

Dimethyl 4-(Methyltio)phenyl Phosphate

```
CH3 - O      O
        \   //
          P
        /   \
CH3 - O      O - methylmercaptophenyl
```

is and insecticide sold under the trade name GC-6506 by Allied Chemical Corp.

1. 14 parts of 4-methyl-mercaptophenol is reacted with 144.5 parts dimethyl chlorophosphate in the presence of a base material like triethylamine, pyridine, or potassium carbonate 14 parts). A catalyst such as copper (.3 parts) may be added to act as a catalyst to accelerate the reaction. The reaction takes place in 50 parts of benzene at 50-60 C.

2. The resulting mix is heated at reflux with continued stirring for 3.5 hours. It is then filtered and the precipitate washed with benzene and then with acetone. Solvent is stripped at reduced pressure leaving the liquid phosphate (65%).

From US Patent 3,151,022 Sept. 1964 assigned to Allied Chemical Corp.

Mevinphos

```
CH3 - O        O
        \    //
          P
        /   \
CH3 - O       O - 2-butenoate
```

is an insecticide and acaricide sold as OS-2046 and Phosdrin (Shell). Its chemical name is Methyl 3-[(dimethoxyphosphinyl)oxy] -2-butenoate.

1. Trimethyl Phosphite (100 grams) is reacted with methyl *a*-chloroacetoacetate 121.5 grams over a one hour reaction period. Temperature rises gradually to 85 C.

2. The reaction mix is then distilled in vacuo with the desired phosphate recovered from boiling at 106-107.5 C at 1 mm of mercury yielding 123 grams of liquid product.

US Patent #2,685,552 assigned to Shell in August 1954.

Monocrotophos

```
CH3 - O        O
        \    //
          P
        /   \
CH3 - O      O - C = C - H
                /     \
             CH3      CNHCH3
                         \\
                          O
```

is an insecticide that is made by reacting trimethyl phosphite with methyl N-methyl methyl-2-chloroacetamide (known as methyl crotonamide).

It si known commercially as C-1414 and Nuvacron (Ciba AG), and SD9129 and Azodrin (Shell). Its chemical name is Dimethyl-1-methyl-3-(methylamino)-oxo-1propenyl phosphate.

Paraoxon

```
C2H5 - O      O
        \    //
          P
        /   \
C2H5 - O      O - p-nitrophenyl
```

is an insecticide with the chemical name - diethyl p-nitrophenyl phosphate. It is sold as E-600 and Mintacol (Bayer) and as Phosphacol. It is made by reacting sodium p-nitrophenate with diethyl phosphate or diethyl phosphorochloridate.

Phosphamidon

```
CH3 - O      O
       \    //
         P             O
       /   \          //
CH3 - O      O - C = CCN - (C2H5)2
                /     \
             CH3       Cl
```

is an insecticide known chemically as 2-chloro-3-(diethylamino)-1-methyl-3oxo-1-propenyl dimethyl phosphate. It is commercially known as Ciba 570 and Dimecron (Ciba-Geigy).

1. Acetoacetic acid diethylamide is treated with sulfuryl chloride (SO2 Cl2) to give *a,a*-dichloroacetoacetic acid diethylamide.

2. This is heated to 93 C (boiling) and is distilled at .18 mm pressure. This is then mixed with trimethyl phosphite at room temperature while heating to 90 C to intitiate the reaction.

3. A violent evolution of gas begins and the reaction heats up to 160 C. When the reaction is finished it is heated under vacuum at 95 C. The pale yellow oily liquid product can be purified by boiling at 162 C under 1.5 mm pressure and distilling off.

From US patent 2,908,605 Oct 1959, assigned to Ciba Ltd.

Stirofos

```
CH3 - O        O
        \    //
          P
        /    \
CH3 -  O      O - C = CHCl
                    \
                     trichlorophenyl
```

is an insecticide, chemical name of 2-chloro-1-(2,4,5-trichlorophenyl)-ethenyl dimethyl phosphate and is sold commercially as SD-8447 and Gardona (Shell) and as Rabon. It is made by

1. Pentachloroacetophenone is prepared by mixing 88 parts aluminum chloride with 109 parts of 1,2,4-trichlorobenzene.

2. To this slurry is added 88 parts of dichloroacetyl chloride while stirring for 10 minutes. This mix is then heated slowly for 4 hours to 90 C. It is then poured onto a mix of ice and hydrochloric acid to decompose the complex.

3. The resulting mix is extracted with ether yielding an organic phase that is washed successively with dilute hydrochloric acid, water, and sodium bicarbonate solutions and finally with a saturated salt solution.

4. The solvent is evaporated off and the residue distilled to yield 134 parts (77% yield) of 2,2,2',4'5'-pentachloroacetophenone, a colorless liquid with a boiling point of 103-105 C.

5. 25.5 parts of trimethyl phosphite is added to 50 parts of the above over 1/2 hour at 30-50 C. After the addition is completed it is heated to 110 C for 1/2 hour.

6. This reaction mixture is then cooled to room temperature and treated with ether to induce crystallization. The formed crystals are cooled in ice and filtered to give 46 parts of a first crop that melts at 97-98 C.

From US Patent 3,102,842 Sept 1963, assigned to Shell Oil Co.

All of the preceding methods of preparing toxic organophosphate esters involve the reacting of prepared intermediate esters. They are all toxic by themselves to some extent and can be made much more toxic by substituting the longer chain (R) with a shorter chain alcohol or by isomerization methods which will be described later. The above methods can be used where a short chain alkane or alcohol can be substituted in place of the long molecules to produce more toxic esters. Part of the science of making pesticides is to combine part of the phosphate with a long chain, usually branched molecule. These materials tend to bind much less cholinesterase in animals and humans and usually find another biological system to affect.

This is important because the human body has only a tiny amount of a neurotransmitter enzyme called acetylcholinesterase. It breaks apart acetylcholine at the rate of about 300,000 per second which is what lets messages get through all parts of the body. These messages are how all our body parts sends signals to all the other parts.

The organophosphorus molecules, depending on their end design, are strongly attracted to one particular spot on this enzyme - where the amino acid serine is located. It combines with the enzyme which prevents it from functioning and sending the body's important signals. The body has only an infinitesimal amount of acetylcholinesterase which makes it possible for only very tiny amounts of nerve agents to tie all the supply up and cause loss of control over all the body's muscles which is what you see happen to insects when they are sprayed with insecticide. Death comes very quickly.

Some of the early observations that could be generalized were that

1. When organophosphates contained short chained, unbranched, alcohols at all positions, they were more toxic and were also more easily absorbed through the skin and other tissues.

2. When longer, branched alcohols or aromatics were attached to at least one of the positions, they were not as easily absorbed by humans and the amounts that were, were less likely to bind to human acetylcholinesterase and often found other biological enzymes to bind to. Usually the human body would have plenty of these other enzymes which is why these types of pesticides are less toxic to people. Insects on the other hand, were found to be in short supply of these other enzymes which causes their deaths quickly. It was also known that are there are small differences in the acetylcholinesterase of insects and other mammals that influenced the toxicity to any particular organophosphate.

One of the possible effects from the blowing up of the Iraqi nerve agents in the Persian Gulf war may have been the reforming of much of the Sarin into less toxic phosphates that may have not been lethal, but would bind in quantity at other biological sites that produce other forms of illness. I will have more to add to this later.

Of the organo "Phosphates" described here, only Phosdrin and Paraoxon have LD 50's of less than 5 PPM making them suitable as a poor mans nerve agent if used undiluted. All the others have LD 50's of 5-50 PPM making the amounts required to be absorbed by contact and necessary to kill, difficult to achieve.

Other toxic phosphate formulas include -

American Cyanamid 4138

```
CH3-O        O
     \      //
        P
      /  \
CH3 - O    O - PhClNO2
```

Dibrom

```
CH3 - O       O
        \   //
          P
        /  \
CH3 - O    O - CBr-H-CBr-Cl2
```

OS 1836

```
CH3 - O        O
        \    //
          P
        /  \
CH3 - O    O-CH=CHCl
```

Phosdrin

```
CH3 - O       O
         \   //
           P
         /  \
CH3 - O     O - CH3C=CCl-CC=ON
                             (C2H5)2
```

Phosphopyristigmine

```
(CH3)2 CH-O          O
           \      //
              P
           /    \
(CH3)2 CH-O      O PhNCH3
```

Ro30340

```
C2H5 - O       O
          \   //
            P
          /  \
C2H5 - O    O - PhN+(CH3)2
```

Ro30351

```
(CH3)2 CH - O        O
            \     //
               P
             /  \
(CH3)2 CH - O     O PhN
```

Ro30412

```
CH3 - O        O
         \     //
            P
          /  \
CH3 - O     O PhN+ (CH3)2
```

Ro30422

```
C2H5 - O      O
         \   //
           P
         /  \
C2H5 - O    O - PhN-Ph
                  \
                   CH3
```

Shell 5539

```
CH3 - O       O
         \   //
           P            O
         /  \          //
CH3 - O     O - C=CHC-CH2Ph
                 \
                  CH3
```

Shell3562

```
CH3 - O        O
        \    //
         P              C
        /  \            //
CH3 - O     O - C=CHC-N-(CH3)2
                  \
                   CH3
```

Stirofos

```
CH3 - O        O
        \    //
         P
        /  \
CH3 - O     O - C=CHCl
                  \
                   Ph-Cl3
```

TOCP

```
OH-Ph-O       O
        \    //
         P
        /  \
OH-Ph-O     O-Ph-OH
```

Phosphonates

```
   X      O
    \    //
      P
     / \
 Y - O   O - Z
```

are characterized by the absence of an oxygen bond at one of the X, Y, or Z positions. One of the components is directly attached to the phosphorus atom. The double bond of the single oxygen atom is also still present. The word "phosphono" in the names of other phosphorus groups represents the lack of an oxygen bond at one of the positions but their may be other differences in other bonds which the name of the group will intend to present.

The phosphonate form of a particular organophosphate is almost always more toxic than its phosphate equivalent. In most cases it is 10-30 times as lethal.

	LD 50 rabbits		LD50 rabbits
(Pr i O)2 P (O) F [DFP]	.45 PPM	(EtO)2 P (O) SCH2CH2NPri2	.08 PPM
(Pr i O) Me P (O) F [Sarin]	.017 PPM	(EtO) Me P (O) " " " [VX]	.009

The bottom line represents the phosphonate form in the above examples. The VX yields the ability to kill at .009 PPM which is only 9 parts per billion (PPB).

Butonate

```
CH3 - O        O
        \    //
          P            O
        /   \         //
CH3 - O       C - HOCC3H7
                \
                  CCl3
```

chemically known as 2,2,2-trichloro-1-(dimethoxyphosphinyl)-ethyl butanoate is an insecticide that is produced by -

1. Add to an Erlenmeyer flask .27 grams of freshly fused and powdered zinc chloride and 29.5 grams of chloral by dripping into a solution of 23.5 grams of n-butyryl chloride.

2. The reaction mixture is placed on a steam bath for 3 hours after which chloral-ethyl-n-butyrate is recovered as an oil by distillation at 100 C at atmospheric pressures.

3. The above is mixed at .1:.1 mol with trimethyl phosphite on a steam bath for about 2 hours. 100 cc of water is then added and the resulting reaction mixture is extracted twice with 100 cc portions of hexane.

4. The solvent is then distilled off yielding the butonate as an oil which is stripped under vacuum to remove any anhydrous butyric anhydride left over.

From US Patents 2,911,435 Nov 1959 and 2,927,881 Mar 1960 assigned to Wisconsin alumni research foundation

Crotoxyphos

```
CH3 - O        O
        \    //
          P
        /   \
CH3 - O       C = C - C - OCH - phenyl
```

is an insecticide with the trade names of SD-4294 and Ciodrin (Shell) and chemical name of 1-phenylethyl (E)-3-[(dimethoxyphosphinyl)oxy]-2-butenoate. It is made by -

Mixing a solution of 20 grams of alpha-methylbenzyl alpha-2-chloroacetoacetate
3 ml of glacial acetic acid
13.65 g of trimethyl phosphite

and allowing it to spontaneously warm to 50 C and is then heated for 4.25 hours at 95-102 C. This mix is then stripped to a kettle temperature of 110 C at .35 mm of mercury to yield 26 grams of product.

US Patents 2,982,686 May 1961 and 3,068,268 Dec 1962 both assigned to Shell Oil Co.

Ethyl Hydrogen 1-Propyl Phosphonate

```
CH2 CH3 - O     O
           \  //
            P
           /  \
CH3 CH2 CH2    O - H
```

is a plant growth regulator that was patented in Aug 1970 in Britain (1,202,442) and assigned to FMC Corp.

It is produced by

1. Mixing a 51.7% dispersion of sodium hydride (34.1 grams) in mineral oil and adding 200 ml anhydrous diethyl ether.

2. 100 grams of diethyl hydrogen phosphite in 200 ml ether is added slowly at a rate to maintain a reflux. Stirring continues until evolution of hydrogen ceases.

3. 89.3 grams of 1-bromopropane is added and heated under reflux overnight.

4. Excess sodium hydride is decomposed by adding a few drops of ethanol and washing the mixture with water. The solution is dried, filtered, and the ether removed by flash distillation.

5. The residue distilled at 88-91 C at 10 mm mercury yielding 45.1 grams.

It can also be made by mixing 37.1 grams of O,O-diethyl propylphosphonate and 150 ml of 10% aqueous sodium hydroxide at 100 C for 2 hours. The solution is cooled in an ice bath, acidified to pH of 4 and then extracted with chloroform. The extracts are dried over anhydrous sodium sulfate and the solvent is removed by flash distillation. The residue is distilled at 106-108 C at .45 mm mercury to yield 10.3 grams.

Glyphosate

```
H - O    O
     \  //
      P              O
     / \            //
H - O   H2 CHNH2 CCOH
```

is a herbicide known by the trade names Mon 0573, Mon 2139, and Roundup (all Monsanto) patented in Mar 1974 US #3,799,758. Its chemical name is N-(phosphonomethyl) glycine.

It is made by 1. Mixing 50 parts glycine, 92 parts of chloromethylphosphonic acid, 150 parts of 50% aqueous sodium hydroxide and 100 parts water and maintaining reflux temperature while 50 more parts of the sodium hydroxide solution is added. pH is maintained at 10-12.

2. The mix is refluxed for an additional 20 hours, cooled to room temperature and filtered.

3. 160 parts of concentrated hydrochloric acid is added and the mix is filtered to yield a clear solution which slowly deposits N-phosphonomethylglycine which melts at 230 C without decomposition.

Trichlorfon

```
CH3 - O     O
        \  //
          P    OH
        / \  /
CH3 - O    C - HCCl3
```

is a widely used insecticide known by the trade names of B-15,922, L 13/59, Dipterex, Neguvon, and Tugon (Bayer), Dylox (Chemagro), and Dyrex, Anthon, Proxol, and Masoten. Its chemical name is Dimethyl 2,2,2-trichloro-1-hydroxyethyl phosphonate. It is made by -

1. Dripping 75 grams of chloral into 60 grams of dimethyl phosphite at a starting temperature of 25 C. This slowly rises to 50 C and is kept between 50-60 C by external cooling.

2. Once cool, the oil is dissolved in benzene and the solution is washed with a sodium bicarbonate solution and dried with anhydrous sodium sulfate.

3. After the solvent is distilled off, the leftover oil almost completely solidifies. It is drawn off and washed with ice cold mixtures of ether and petrol ether. The 90 grams of colorless needle crystals have a melting point of 81 C.

All of the phosphonates listed here have relatively low toxicity in the presented form except for Crotoxyphos which has an oral LD50 of 15-22 ppm in mice and a dermal LD50 of 225 PPM in rabbits.

Other toxic phosphonate formulas include -

Dipterex

```
CH3 - O        O
        \    //
          P
        /   \
CH3 - O      CH-CCl3
               \
                OH
```

Phosphonofluoridates

```
  X     O
   \   //
     P
    / \
Y - O   F
```

are characterized by the absence of an oxygen atom to connect X or Y (the phosphono classification), the presence of the fluorine atom at the 3rd (lower right) position, and the double bond P=O. The phosphonofluoridates are among the most potent cholinesterase inhibitors making them the best candidates as a group for use as nerve gas weapons.

The Germans had difficulty manufacturing Sarin or Soman at first. The reason for this is that the element fluorine attached to the acid phospho material causes it to attack glass and almost all other metals. Since most manufacturing of chemicals is done with glass lined vessels, pipes, and shells, it was impossible to use the ordinary types of contact surfaces to control corrosion. All the phosphonofluoridates would eat their way through the glass, and then the metal, and then would leak into the plant killing the workers. Corrosion studies finally found that using silver lining as the principal contact surface would allow a safe method of production. It came too late in the war for the Sarin (and Soman) plants to be completed. Modern engineering materials have since been invented that are highly resistant to both the high temperatures of reaction and the corrosive effects of fluorine and phosphorus type acids. These include many materials which already incorporate fluorine in its structure such as Teflon.

[Authors note - I have had personal experience in this regard. The phosphoric acid plants that I designed used hydrochloric acid attack and high surface area silica (diatomaceous earth) to remove fluorine from the rock and acid phosphates to make them safe for animal feeds. I had several patents filed for regarding these processes and was weeded out from obtaining them by the sheer cost and trouble that the government makes everyone go through. The diatoms made of silica would gobble up the fluorine forming a variety of SiF compounds that we could filter or volatalize out of the feed material. Glass is also made of silica and readily reacts with the fluorine, especially at boiling temperatures.]

Sarin

```
        CH3   O
          \  //
            P
           / \
CH3CHCH3     F
```

A large rate constant above means an less stable molecule. Increasing the size of R' from methyl to ethyl and then to isopropyl increases the stability considerably and makes it much more persistent on the battlefield. The term "Cyclo Sarin" used in the press refers to the use of "cyclic-closed ring" organic compounds at the R' position to increase the persistence even further. All the above analogues have toxicities similar to Sarin.

Soman

```
          CH3   O
            \   //
   CH3        P
    \        / \
   C - CH - O    F
```

is similar to Sarin with Pinacolyl alcohol used in place of isopropyl alcohol to effect the transfer of Y - O. This alcohol has the structure of

```
   CH3   CH3
     \   /
       C     OH
      / \   /
   CH3  CH - CH3
```

This is also known as 3,3,-dimethyl-2-butanol.

Most of the short chain unbranched alcohols make deadly phosphonofluoridate nerve agents and as is seen in the formula of Soman above, some of the branched chains can be deadly as well. Soman kills at about 1/3 the dose of Sarin or about .006 PPM (LD50-Rat).

Some binary weapons have been constructed using

Methylphosphoryldifluoride (DF) and isopropanol as the two components to yield Sarin (GB-2) when both are mixed together. The reaction is accelerated by external heating.

Methylphosphoryldifluorid and pinacolyl alcohol are reacted to yield Soman (GD-2).

The yields of these weapons depends on complete reaction which is not accomplished in battlefield conditions instantly. Arranging a mixing action substantially prior to use will help acheive complete yields and more effective matreial concentrations being released on the battlefield.

Phosphorothionates

```
X - O      S
     \   //
       P
     /   \
Y - O     O - Z
```

are characterized by the double bonded sulfur atom in place of the oxygen atom in the phosphates. Those phosphorus compounds that have sulfur as an attached atom to the phosphorus are designated "thio" substances. All the other positions have a single bonded oxygen atom attached to the phosphorus and are themselves bonded to an X, Y, and Z component.

Bromophos

```
CH3 - O       S
       \    //
         P       Cl
       /   \    //  \\
CH3 - O     O -        - SCH3
                \ ---/
                     Cl
```

chemically known as O-(4-bromo-2,5-dichlorophenyl)-O,O-dimethyl phosphorothioate was patented on Sept 27,1966 by R. Sehring and Zeile and is assigned to C.H. Boehringer Sohn. [#3,275,718]

It is produced by -

1. Suspending 272.9 grams of 2,5-dichloro-bromophenyl sodium (1 mol) in 700 cc of chlorobenzene and admixing into this solution 176.66 grams of O,O-dimethyl-thiophosphoric acid chloride (1.1 mol).

2. Potassium bromide (5 grams) is added as a catalyst.

3. The resulting mixture is heated for 8 hours at 100 C while stirring.

The sodium chloride precipitate is filtered off and the filtrate is washed with dilute sodium hydroxide and dried over sodium sulfate. The chlorobenzene is distilled off and a colorless oil remains which crystallizes into 95% Bromophos. It can be purified by distillation or recrystallization from methanol. The pure material has a M.P of 51 C and boils at 140-142 C at .01 mm Hg.

Bromophos Ethyl

```
CH3 CH2 - O          S
            \      //
              P        Cl---
            /    \    /    \
CH3 CH2 - O        O -        - Br
                      \ __ //
```

also known as Bromopropylate - O-(4-bromo-2,5-dichlorophenyl)-O,O-diethyl phosphorothioate is made using the same procedure as Bromophos with 272.9 grams of 2,5-dichloro-4-bromo-phenyl sodium reacted with 186.5 grams of O,O-diethyl-thiophosphoric acid chloride to form 380 grams (96% of theoretical) of the final product.

It was patented by the same scientists on the same day as Bromophos (#3,275,718).

Chloronitrophenyl Dimethyl Phosphorothionate

```
CH3 - O        S
        \    //
          P
        /   \
CH3 - O       O - Chloronitrophenyl
```

Patented by Gerhard Schrader (U.S. Patent # 2,701,259) on Feb. 1, 1955 and assigned to Farbenfabriken Bayer AG, it is produced by -

1. Suspending 87 grams of 4-nitro-3-chlorophenol in 300 cc of methyl ethyl ketone with 80 grams of powdered and sifted potassium carbonate and adding 2 grams of copper powder.

2. Add 81 grams of O,O-dimethyl chlorothionophosphate at 65 C while stirring and refluxing.

3. The exothermic reaction is kept at 70 C for one hour and the separated salt is removed by filtration. The filtrate is vacuum distilled to separate the product from solvent. The remaining oil is then heated for 10 minutes at 1mm Hg at 90 C. An 89% yield of 132 g of the light yellow, water insoluble oil is produced.

Chlorpyrifos

```
C2H5 - O       S
          \    //
            P
          /   \
C2H5 - O     O - 3,5,6-trichloro-2-pyridyl
```

Patented in April 5, 1966 (#3,244,586) by Rigterink and assigned to Dow chemical, it has become a popular insecticide under the trade names Dowco 179, Dursban, and Lorsban. Its many methods of manufacture give good insights into to general chemistry and production methods of this class of organophosphates.

The preferred method described in the literature is -

1. Taking a phosphorochloridate or phosphorochlorodithioate with the structure

```
R      Z
  \   //
    P
  /   \
R      Cl
```

and reacting it with an alkali metal or tertiaryamine salt of a halopyridinol with the formula of -

R - O - alkali metal   or   R - OH - Tertiaryamine

The reaction proceeds in inert solvent (acetone, dimethyl formamide, carbon tetrachloride, chloroform, benzene, toluene, isobutyl methyl ketone, or methylene dichloride) and any amounts of either reactants will yield some of the final product. They react at 0 - 100 C with equimolar amounts being normally used to yield the final product and a byproduct chloride salt.

Another route to making it is to react a phosphorodichloridate or dithionate with this structure -

```
             Cl      Z
               \   //
                 P
               /   \
lower alkoxy      Cl
```

with an alkali metal salt of a halopyridinal to form an intermediate of -

```
              R - O        Z
                   \      //
                      P
                     / \
       lower alkoxy     Cl
```

This intermediate is then reacted with ammonia or a lower alkyl amine to produce the desired phosphoramidate or phosphoramidothioate. The reaction again is carried out in one of the inert substances mentioned above. This reaction is exothermic and is carried out at -50 to 25 C.

You can control the rate of additions or externally cool to maintain these temperatures. The byproducts of both reactions is an alkali metal chloride (salt) or tertiaryamine chloride from the ammonia or amine reactant.

The reaction is washed with water and the organic reaction solvent is removed by fractional distillation under reduced atmospheric pressure (vacuum). The remaining residue can be further purified by washing with water and dilute caustic soda, solvent extracted, and recrystallized.

An alternative is to react phosphorus oxychloride or thiochloride with a halopyridinol salt to form the intermediate halopyridinol phophorodichloridate or dithioate. These can be reacted with an alkali metal alcoholate (sodium methylate) or ammonia, or a lower alkylamine (in stages) to produce the desired monoester, diester, or triester.

Other phosphorothionates include -

Chlorpyrifos Methyl, Patent # 3,244,586, April 5, 1966, aasigned to Dow Chemical
Coumaphos, Pat # 2,748,146, May 29, 1956 assigned to Farbenfabriken Bayer AG (Schrader)
Cyanophos, Pat# 3,150,040, Sept 22, 1964 assigned to Sumitomo Chemical Co. Ltd.
Demephion, Pesticide manual 4th Edition p155, Nov 1974.
Demeton, Pat #'s, 2,571,989, Oct 16, 1951, & 2,597,534, May 20, 1952 assigned to Farbenfabriken Bayer AG (Schrader) and **Demeton-Methyl** - Pesticide Manual 1974.
Diazinon, Pat # 2,754,243, July 10, 1956 assigned to J.R. Geigy AG.
Dicapthon, Pat# 2,784,207, March 5, 1957 assigned to American Cyanamid Company
Dichlofenthion, Pat# 3,004,054, Oct 10, 1961 assigned to Virginia-Carolina Chemical Corp.
Diethyl Methyl Coumarinyl Phosphorothioate, Pat# 2,583,744, January 29, 1952 assigned to Farbenfabriken Bayer AG (Schrader)
Ditalimfos, British patent # 1,034,493, June 29, 1966
Famfor, Pat# 3,005,004, October 17, 1961 assigned to American Cyanamid Co.
Fenitrothion, Pesticide Manual pg 269, Nov 1974.
Iodofenphos, Pesticide Manual pg 303, Nov 1974.
Methyl Parathion, Pat #'s 2,624,745 Jan 6, 1953 assigned to Farbenfabriken Bayer AG (Schraden); 2,663,721 assigned to Monsanto Chemical Co., 2,471,464 May 31, 1949 assigned to Victor Chemical Works
Omethoate, Pesticide manual pg 382, Nov 1974.
Oxy Demeton Methyl, Pat#'s 2,791,599, May 7, 1957, assigned to Pest Control Ltd, and 2,963,505, Dec 6, 1960, assigned to Farbenfabriken Bayer AG.
Parathion, Pat #'s 1,893,018, Jan 3, 1933, assigned to American Cyanamid Co., 2,482,063, Sept 13, 1949 assigned to American Cyanamid Co., 2,663,721, Dec 22, 1953, assigned to Monsanto Chemical Co.
Phoxim, Pesticide Manual pg 410, Nov 1974.
Pirimiphos-ethyl, British Pat#'s 1,019,227, Feb 2, 1966, assigned to Imperial Chemical Industries, and 1,205,000, Sept. 9, 1970 assigned to Imperial Chemical Industries, and US Patent 3,287,453, Nov 22, 1966 assigned to Imperial Chemical Industries.
Prothoate, Pat # 2,494,283, Jan 10, 1950 assigned to American Cyanamid Co.
Pyrazophos, Pat# 3,496,178, Feb 17, 1970 assigned to Farbwerke Hoechst AG.
Quinalphos, Pesticide Manual pg 439, Nov 1974.
Ronnel, Pat #'s 2,599,515 and 2,599,516, June 3, 1952 assigned to Dow Chemical Co.
Thionazin, Pat#'s 2,918,468, Dec 22, 1959 and 2,938,831, May 31, 1960 assigned to American Cyanamid Co.
Triazophos, Pat# 3,686,200, Aug 22, 1972, assigned to Farbwerke Hoechst AG.

Organic Additives and Reactants

An incredible number of organic compounds are known and can be reacted with and attached to the phosphorus molecules. These organics are usually represented by the letter R or R' when used in a phosphorus formula. This usually means that any of the organic materials we are about to describe may be substituted in place of R. Some 10 million organic compounds have already been identified, named and described in the abstracts. Combined with phosphorus in all possible combinations, the possibilities would probably number in the billions. The categories of organic materials are given different names to represent their different structures as follows -

I. Aliphatic (straight chain)

1. Hydrocarbons that are derived from petroleum and coal
    - a) Paraffin's or alkanes (saturated - $C_n H_{2n+2}$), methane and homologs and halogen substituted derivatives like fluorocarbons.
    - b) Olefins (unsaturated)
        includes Alkenes ($C_n H_{2n}$) ethylene and homologs, and
        Alkadienes ($C_n H_{2n-1}$) butadiene, allene
    - c) Acetylene's or alkynes

2. Alcohol's (ROH) such as methanol and ethanol and homologs
3. Ethers (ROR) such as methyl ether and homologs
4. Aldehydes (RCHO) such as formaldehyde and acetaldehyde
5. Ketones (RCOR) such as acetone and methylethyl ketone
6. Carboxylic acids (RCOOH)
7. Carbohydrates ($C_n H_{2n} O_n$) includes sugars, starches, and cellulose.

II. Cyclic (closed ring)

1. Alicyclic hydrocarbons
    - a) Cycloparrafins like cyclohexane and cyclopentane
    - b) Cycloolefins like cyclopentadiene and cyclooctatetraene
    - c) Cycloacetylenes

2. Aromatic hydrocarbons (arenes)
    - a) Benzene group (1 ring)
    - b) Naphthalene group (2 rings)
    - c) Anthracene group (3 rings)
    - d) Polycyclic group (4 rings steroids and sterol)

3. Heterocyclic containing at least one other element besides carbon and hydrogen.
    - a) pyrroles
    - b) furans
    - c) thiazoles
    - d) porphyrins

III. Combinations of aliphatic and cyclic structures
1. Terpene hydrocarbons
2. Amino acids
3. Proteins and nucleic acids

IV. Organometallic compounds

V. Synthetic high polymers including silicones

The word homologs in the above descriptions means that in the particular series of compounds, each successive member has one more CH2 group in its molecule than the preceding member. For example, in the alcohols -

Methanol	CH3 OH
Ethanol	C2H5 OH
Propanol	C3H7 OH

all form a homologous series that goes on into the hundreds of possible extended compounds.

In organic chemistry, the names of the functional groups and examples of them include -

Hydrocarbons			
Alkanes	Ethane	CH3CH3	R R
Alkenes	Ethylene	CH2=CH2	R=R
Alkynes	Acetylene	HC=CH	
Dienes	1.3 Butadiene	CH2=CHCH=CH2	
Arenes	Benzene	C6H6 (ring)	
Halogen substituted derivatives of hydrocarbons			
Alkyl halides	Ethyl Chloride	CH3 CH2 Cl	R Cl (or X)
Alkenyl halides	Chloroethane	CH2=CHCl	
Aryl Halides	Chlorobenzene	C6H5Cl	
Oxygen containing organic compounds			
Alcohol's	Ethanol	CH3CH2 OH	R OH
Phenols	Phenol	C6H5 OH	R OH
Ethers	Diethyl ether	CH3CH2 O CH2 CH3	R O R
Epoxides	Ethylene Oxide	(CH2)2 O	R2 COC R2
Aldehydes	Acetaldehyde	CH3 CH O	R COH
Ketones	Acetone	CH3 CO CH3	R CO R
Carboxylic acids	Acetic acid	CH3 CO OH	R CO OH

Carboxylic Acid Derivatives

Acyl halides	Acetyl chloride	CH3 CO Cl	R CO X
Acid Anhydrides	Acetic anhydride	CH3 CO O OCCH3	R COOOC R
Esters	Ethyl Acetate	CH3 CO O CH2CH3	R CO OR
Amides	*N*-methylacetamide	CH3 CO NHCH3	R CO NR2

Nitrogen containing organic compounds

Amines	Ethylamine	CH3 CH2 NH2	R NH2
Nitriles	Acetonitrile	CH3C N	R CN
Nitro compounds	Nitrobenzene	C6 H5 NO2	R NO2

Sulfur containing organic compounds

Thiols	Ethanethiol	CH3 CH2 SH	R SH
Sulfides	Diethyl Sulfide	CH3 CH2 SCH2 CH3	R S R

Don't worry about memorizing a lot of formulas. You can always look them up to see what they are called and what group they belong to. The above list gives you the name of the group and general chemical description so you have an idea of what the name represents when we use it later in the phosphorus formulas and charts.

The unbranched alkanes or alcohols are common materials used to make nerve agents. The names for these materials and the number of carbon atoms are listed as follows -

1	Methane	CH3
2	Ethane	C2H5
3	Propane	C3H7
4	Butane	C4H9
5	Pentane	C5H11
6	Hexane	C6H13

and so on into the hundreds of carbon atoms (100 = hectane)

The *n*-alkanes are characterized by having a methyl group at both ends of a continuous series of methylene groups. This is written out as -

n-pentane	CH3 CH2 CH2 CH2 CH3
n-hexane	CH3 CH2 CH2 CH2 CH2 CH3

and so on.

It is possible for the groups to be arranged in what are called isomers. Some of the isomers of the organophosphates are very much more toxic than their parent chemical and this will be taught later in this chapter.

[Author note - Ethylene is obviously the ethanol without the OH or water of hydration. I have been asked how you dehydrate ethanol (from corn distillation) into ethylene since it is important in making things like mustard and nitrogen mustard and the various nerve agents. Around the time of our revolutionary war, backwoodsmen discovered that by passing the distilling ethanol gas through a pipe or column packed with silica gel or alumina, it would remove the water and dehydrate the ethanol to ethylene as it condensed into the next cooling stage. The silica gel or alumina is the same stuff you see in the shipping packages that are used to keep shipments of electronics dry. In modern production, these are combined with phosphoric acid to maximize dehydration efficiency.]

Phosphates

are compounds which contain P - O linkages, Usually these are 3, 4, or 5 oxygen atoms linked directly to a central phosphorus atom. The O will often be linked with an R (organic) compound as well -

```
R - O                  O   O          R - O   O - R
     \                  \ /                \ /
R - O - P                P                  P
     /                  / \                / \
R - O                  O   O          R - O   O - R
```

Orthophosphates are regularly encountered in agricultural phosphate chemistry. The single oxygen is double bonded -

```
O     O
 \  //
   P
  / \
 O   O
```

Condensed phosphates are organized around 2 or more phosphorus atoms and can also make very toxic materials (P2 O7)

```
   -O         O
     \       //
 -O - P - O - P - O -
     //       \
    O          O
```

Chains of condensed species can be formed continuously with the ratio of P to O narrowing.

Orthophosphoric acid is the above left formula with the O attached to an H at the three single bonded oxygen atoms.

The oxy acids of phosphorus that are best known and most used are -

```
 Phosphoric        Phosphorous        Hypophosphorus      Pyrophosphoric
 H-O   O           H     O            H     O             H - O  O      O
    \ //              \ //               \ //                   \ //    //
     P                 P                  P               H - O- P - O - P - O -H
    / \               / \                / \                    /       /
H - O   O - H    H - O   O - H          H   O - H         H - O  H - O
```

```
Phosphorus acid may also exist as a phosphite -       HO
                                                        \
Phosphites are powerful reducing agents and are       HO - P
used widely in preparing nerve agents                    /
                                                      HO
```

Phosphorus and Carbon Compounds

Materials that contain carbon and phosphorus are known as organophosphates. Most of these have P - O - C linkages which have esters (organic molecules as part of the C link) attached and are called phosphate esters.

Most of the organic phosphate esters have the following structures -

```
R          R          R   X
 \          \          \ //
  P       R - P         P
 //          /         / \
R          R          R   R
```

When the formula for the material is PH3 it is called Phosphine
R P (OH)2 is called phosphonous acid
R2 POH is called Phosphinous acid

Esters of phosphonous and phosphinous acids are used in producing many toxic phosphate nerve agents. These are called -

Phosphonates HPO (OR)2
Phosphinates H2P (O) OR

Metal phosphides can be reacted directly with alkyl halides to form phosphines -

NaPH2	+ RX =	R PH2 + NaX
NaPHR	+ R'X =	R R' PH + NaX
NaPr2	+ R'X =	R2 PR' + NaX
Na3 P	+ 3RX =	R3P + 3NaX

A general description for the main compounds containing one phosphorus atom and relevant to weapons production are -

```
Phosphoric Acid     Ethyl Phosphate     Diethyl Phosphate     Triethyl Phosphate
HO    O             EtO    O            EtO    O              EtO    O
  \  //               \  //               \  //                 \  //
   P                   P                   P                     P
  /  \                /  \                /  \                  /  \
HO    OH            HO    OH            EtO    OH             EtO    OEt
```

```
Diethyl Phosphonate        Diethyl Methyl Phosphonate
EtO    O                   Me     O
  \  //                      \  //
   P                          P
  /  \                       /  \
EtO    H                   EtO    OEt
```

```
Phosphonic Acid     Methylphosphonic Acid
HO     O            Me     O
  \  //               \  //
   P                   P
  /  \                /  \
 H    OH            HO    OH
```

```
Ethyl Phosphonic Acid      Ethyl Methyl Phosphonate
EtO    O                   EtO    O
  \  //                      \  //
   P                          P
  /  \                       /  \
 H    OH                   Me     OH
```

```
Phosphinic Acid     Methyl Phosphinic Acid     Dimethylphosphinic Acid
H      O            Me     O                   Me     O
 \   //               \  //                      \  //
   P                   P                          P
  /  \                /  \                       /  \
 H    OH             H    OH                   Me     OH
```

Ethyl Phosphinate
```
H      O
 \    //
   P
  / \
EtO  H
```

Ethyl Methylphosphinate
```
Me     O
  \   //
   P
  / \
EtO  H
```

Ethyl Dimethylphosphinate
```
Me     O
  \   //
   P
  / \
Me    OEt
```

Methylphosphonous Acid
```
       OH
      /
Me - P
      \
       OH
```

Ethyl Methylphosphonite
```
       OEt
      /
Me - P
      \
       OH
```

Diethyl Methylphosphonite
```
       OEt
      /
Me - P
      \
       OEt
```

Monomethyl Phosphinous Acid
```
Me
  \
   P - OH
  /
 H
```

Ethyl Monomethylphosphinite
```
Me
  \
   P - OEt
  /
 H
```

Dimethyl Phosphinous Acid
```
Me
  \
   P - OH
  /
Me
```

Ethyl Dimethylphosphinite
```
Me
  \
   P - OEt
  /
Me
```

Monoethyl Phosphite
```
EtO
   \
    P - OH
   /
 HO
```

Diethyl Phosphite
```
EtO
   \
    P - OH
   /
 EtO
```

Triethyl Phosphite
```
EtO
   \
    P - OEt
   /
 EtO
```

```
Phosphonic Halides          Phosphinyl Halides
R     O                     R     O
 \   //                      \   //
   P                           P
  / \                         / \
 X   X                       R   X
```

are also important intermediates for producing toxic organophosphates. They can be produced by reacting the corresponding phosphonic or phosphinic acids listed earlier with the desired alkyl (R) and halogen (X).

They can also be prepared by reacting

	RP (O) (OH)2 + 2 PCl5	=	RP (O) Cl2 + 2 POCl3 + HCl
or	R2P (O) OH + SoCl2	=	R2P (O) Cl + SO2 + HCl

You can also produce these halides by reacting phosphonate and phosphinate esters -

	MeP (O) (OMe)2 + 2 PCl5	=	MePOCl2 + 2 POCl3 + 2MeCl
or	CH2=CH.P (O) (OEt)2 + 2 PCl5	=	CH2=CH.POCl2 + 2POCl3 + 2MeCl

You can use a slurry of phosphorus pentoxide and halophosphine -

6RPCl2 + 6Cl + P2O5 = 6 RPOCl2 + 4 POCl3

You can also oxidize a phosphonous halide with sulfuryl chloride or oxygen -

	EtPCl2 + SO2 Cl2	=	EtPOCl2 + SOCl2
and	PhPCl2 + 1/2 O2	=	PhPOCl2

You can heat aldehydes with phosphorus trichloride at 200 C -

PCl3 + RCHO = R.CHCl.POCl2

You can add phosphorus pentachloride to alkenes and alkynes which form complexes that can be treated with sulfur dioxide to yield phosphonyl chloride -

PhCh=CH.P+Cl3 / PCl6 + 2 SO2 = PHCH=CH.POCl2 + POCl3 + 2SOCl2

Reacting phosphinyl halide with metal cyanates produces very reactive cyanate compounds -

```
Me    O                          Me    O
  \  //                            \  //
   P        + Na OCN   =            P        + NaCl
  / \                              / \
Et    Cl                         Et    NCO
```

Phosphonous and phosphinous acids are used to make a variety of important esters -

```
    OH              R     O
   /                 \   //
R - P                  P
   \                  / \
    OH              HO   H
```

Hypophosphite esters are added directly to olefins, aldehydes, and ketones -

RCH=CH2 + H2P(O)OR = RCH2CH2 P (O) (H) OR

Triaryl phosphites and grignard reagents produce 30-50% yields with phosphorohalidites -

(RO)3 P + R'MgX = R'P(OR)2 + Mg(OR)X

(RO)2 PX + R'MgX = R'P(OR)2 + MgX2

Alcohol's acting directly on phosphonous diamides yield -

RP(NR2)2 + 2R'OH = RP(OR')2 + 2RNH

Phosphonoamidous esters, or phosphonous dichloride's with a base like triethylamine or pyridine to remove HCl, and alkoxides all react to yield **phosphonous esters** -

RP (NR2)OR' + R"OH = RP (OR') OR" + R2NH

RPCl2 + 2R'OH + 2R'OH + 2 Et3 N = RP(OR)2 + 2 Et3 N.HCl

RPCl2 + 2R'ONa = RP(OR')2 + 2NaCl

Difluorophosphine and methanol yield dimethyl phosphonite directly -

PF2H + 2 MeOH = (MeO)2 PH + 2HF

Phosphonous diesters are easily oxidized on exposure to air -

```
RP (OR)2 + 1/2 O2   =       R      O
                             \    //
                               P
                             /  \
                           RO    OR
```

Sulfur reacts directly to yield **phosphonothiionic esters** -

```
RP (OR)2 + S        =       R      S
                             \    //
                               P
                             /  \
                           RO    OR
```

The esters can sometimes be swapped by heating an alcohol or glycol with a diester -

RP (OR)2 + 2R"OH = RP(OR') (OR") > RP (OR")2 + 2R'OH

Phosphinous esters can be made by adding a phenol or alcohol to a dialkyl or diaryl chlorophosphine in the presence of a base like pyridine or triethylamine -

R2PX + R'OH + Et3N = R2POR' + Et3N.HX

Phosphinic esters are very important intermediates because their P-H bonds are so reactive

```
H      O
 \    //
   P
 /  \
R    OR
```

These are made from reacting alcohols at ice cold temperatures with phosphinous dichloride's

RPCl2 + 2R'OH = RPH (O) OR' + R'Cl + HCl

The low temperature is necessary to prevent cleavage of the second ester group.

Phosphonic acids may be converted directly to esters with alcohol -

RPO (OH)2 + 2ROH = RPO (OR)2 + 2 H2O

Dimethyl methylphosphonate may be used directly as a methylating agent in converting certain organophosphate pesticides to potent nerve agents. (See last section of this chapter)

Phosphorus trichloride can be reacted directly with alcohols to yield **trialkyl phosphites** -

$$PCl_3 + 3\ ROH \quad = \quad (RO)_3P + 3\ HCl$$

By mixing methanol with higher alcohols at -5 C, **dialkyl hydrogen phosphites** may be formed -

$$PCl_3 + 2\ ROH + MeOH \quad = \quad (RO)_2\ POH + MeCl + 2\ HCl$$

The methyl and hydrogen chlorides are separated out by heating under vacuum.

Trialkyl phosphites and phosphorus trichlorides can be mixed together forming an exchange reaction -

$$(RO)_3P + PCl_3 \quad = \quad ROPCl_2 + (RO)_2\ PCl$$

This is important because the direct hydrolysis of the above chloridites yields phosphonates -

$$(EtO)_2PCl + H_2O \quad = \quad (EtO)_2\ P\ (O)\ H + HCl$$

The reactions of triesters allows the formation of many intermediates that are used in production of nerve agents and which are described in the reaction instructions for each group later in this chapter. The main reactions are -

$(RO)_3\ P$	+	R'X	=	$(RO)_2\ P\ (O)\ R'$
		heat		$(RO)_2\ P\ (O)\ R$
		N_2O_4, SO_2		$(RO)_3\ PO$
		S		$(RO)_3\ PS$
		R'SSR'		$(RO)_2\ P\ (O)\ SR'$
		R'SCl		$(RO)_2\ P\ (O)\ SR'$
		R'SH		$(RO)_3\ PS$
		R'OH		$(R'O)_3\ P$
		R'MgX		$R_2'P(O)R$
		Cl_2		$(RO)_2\ P\ (O)\ Cl$
		PCl_3		$ROPCl_2 + (RO)_2\ PCl$
		HCl		$(RO)_2\ P\ (O)\ H$
		$H_3\ PO_3$		$(RO)_2\ P\ (O)\ H$
		NH_3		$(RO)_2\ P\ (O)\ NHR$
		RCOOH		$(RO)_2\ P\ (O)\ H$
		$CH_2=N=N$		$(RO)_3\ P=N=N=CH_2$

All **phosphites** can be isomerized simply by heating but many of these compounds are unstable. The R = Me reaction converts completely at 200 C in 18 hours.

```
RO                       RO    O
   \                       \  //
RO -  P        >             P
   /                       /  \
RO                       RO    R
```

Under mild acid or alkaline conditions, phosphite triesters hydrolyze to dialkyl phosphonates -

```
(RO)3 P + H2O     =     (RO)2 P = O        + ROH
                                \
                                 H
```

All phosphates can be oxidized partially by air and completely by oxygen, hydrogen peroxide, ozone, dinitrogen tetroxide, alkyl hypochlorites, amine oxides, sulfur dioxide, and sulfuryl chloride. Heating triethyl phosphite with di-tertiary butyl hydroxide yields triethyl phosphate -

But O-OBut + (EtO)3 P = (EtO)3 PO + Me3 C-CMe3

Dialkyl Phosphonates are formed from mixing phosphorous acid and trialkyl phosphites -

```
(RO)3 P + H3 PO3    =    (RO)2P =O    +    RO    O
                               \             \  //
                               H               P
                                              /  \
                                            HO    H
```

They are neutral materials that do not react with most bases to form salts and are not easily oxidized. They can be made to react with alkali metals in organic solvents to form salts and evolve hydrogen. They can undergo many reactions, some of the important ones in organophosphates are listed here -

(RO)2 P (O) H	+	NaOH + CCl4	=	(RO)2 P (O) OP (O) (OR)2
		NaOH		(RO)2 POONa
		CCl4 + NaCN		(RO)2 P (O) CN
		R'NH2 + CCl4		(RO)2 P (O) NHR
		ArOH + CCl4		(RO)2 P (O) Ar
		R'OH + CCl4		(RO)2 P (O) OR

$(RO)_2P(O)H$	+	H_3PO_3	=	$(RO)(HO)P(O)H$
		SO_3, N_2O_4		$(RO)_2P(O)OH$
		Cl_2		$(RO)_2P(O)Cl$
		$R'OH$		$(R'O)_2P(O)H$
		S_2Cl_2		$(RO)_2PSSP(OR)_2$

When the dialkyl phosphite is reacted with sodium metal in organic solvent the product and its reactions are -

$(RO)_2P(O)H + Na =$

$(RO)_2PONa$	+	$(R'O)_2POCl$	=	$(RO)_2P(O)(OR')_2$
		Cl_2		$(RO)_2PCl$
		H_2O		$(RO)P(O)H(ONa)$
		S		$(RO)_2P(S)ONa$
		$R'SSR'$		$(RO)_2P(O)SR'$
		$R'X$		$(RO)_2P(O)R'$
		$R'SCl$		$(RO)_2P(O)SR'$

Phosphorus-Nitrogen compounds are considered to be mainly derived from

1. Phosphorus Triamide/ Triamino phosphine	$(NH_2)_3P$
2. Tetra aminophosphonium	$(NH_2)_4P$
3. Phosphorus Pentamide/ Penta aminophosphorane	$(NH_2)_5P$
4. Hexa aminophosphoride	$(NH_2)_6P$

Most of the oxy derivatives are produced from phosphoric, phosphonic, or phosphinic acids by the replacement of OH with NH_2. The hydrogen atoms in these groups can also be replaced by halogens, sulfur in thio substances or other organics which give rise to enormous numbers of compounds based on these arrangements. The major classes of these compounds are -

Phosphinous Amide	R_2PNR_2
Phosphonous Diamide	$RP(NR_2)_2$
Phosphoramidite Ester	$(RO)_2PNR_2$
Phosphorodiamidite Ester	$(RO)P(NR_2)_2$
Phosphoramidous Halide	R_2NPX_2
Phosphorodiamidous Halide	$(R_2N)_2PX$
Phosphonamidous Halide	$RP(NR_2)X$
Phosphorus Triamide	$P(NR_2)_3$
Phosphinic Amide	$R_2P(O)NR_2$
Phosphoric Diamide	$RP(O)(NR_2)_2$
Phosphoramidate Ester	$(RO)_2P(O)NR_2$

Phosphoramidic Halide	$R_2N\ P\ (O)\ X_2$
Phosphorodiamidic Halide	$(R_2N)_2\ P\ (O)\ X$
Phosphonamidic Halide	$RP\ (O)\ (NR_2)\ X$
Phosphoric Triamide	$P\ (O)\ (NR_2)_3$

Phosphorus triamide is prepared by reacting ammonia and phosphorus trichloride at low temperature (see chart of PCl_3 reactions). Tetra aminophosphonium chloride is prepared from ammonia and PCl_3 at -170 C and below.

Phosphoramidates and phosphorodiamidates are prepared from reacting ammonia with the corresponding phenyl phosphorochloridates made from reacting phenol with phosphorus oxychloride -

$(PhO)\ POCl_2 + 4\ NH_3$	=	$(PhO)\ PO\ (NH_2)_2 + 2NH_4Cl$
$(PhO)_2\ POCl + 2\ NH_3$		$(PhO)_2\ PO\ (NH_2) + NH_4Cl$

Phosphonic diamide $HP\ (O)\ (NH_2)_2$ is made by dissolving phosphorus trioxide in benzene and saturating it with ammonia. The reactive white powder dissolves in water and yields enough heat to produce incandescence.

Phosphoric Triamide $PO\ (NH_2)_3$ is made by mixing ammonia with phosphoryl chloride or triphenyl phosphate.

A condensed species, Pyrophosphoric tetramide is a colorless odorless solid that can be prepared in 89% yield by reacting pyrophosphoryl chloride or fluoride with liquid ammonia.

Heating dry phosphoric triamide will also yield a variety of condensed species, some of which are useful in producing toxic end products.

Phosphorus Trichloride reacts with dimethylamine to produce tris deimethylaminophosphine ($P\ (NMe_2)_3$. The important reactions are -

$P\ (NMe_2)_3$	+	O	=	$P\ (O)\ (NMe_2)_3$
		S		$P\ (S)\ (NMe_2)_3$
		X_2		$P\ (NMe)_{23}\ X+\ X-$
		$NH_2\ Cl$		$P\ (NMe_2)_3\ NH_2^+\ Cl^-$
		MeI		$P^+\ (NMe_2)_3\ Me\ I^-$
		PhN_3		$(Me_2N)_3\ P{:}NPh$
		$Ph\ NH_2$		$P\ (NMe_2)\ (NHPh)_2$
		PCl_3		$PCl\ (NMe_2)_2 + PCl_2\ NMe_2$
		HBr		$PBr\ (NMe_2)_2$
		B_2H_6		$(Me_2N)_3\ PBH_3$
		$Ni\ (CO)_4$		$Ni\ (CO)_2\ [PN\ (Me_2)_3]$
		EtOH		$P\ (OEt)_3$

The last reaction is actually a transesterification which can be done with all alcohols -

(Me2N)3 P + 3 EtOH = 3 Me2 NH + P (OEt)3

The phosphoramidic dichloride's react with alcohol, primary amines, and ammonia to yield phosphoramidates or phosphoryl amides -

Me2N.POCl2 +	2 EtOH	=	Me2N.PO (OEt)2 + 2 HCl
Me2N.POCl2 +	2 NH3		Me2N.PO (NH2)2 + 2 HCl
ME2N.POCl2 +	Et NH2		Me2N.PO (NH Et)2 + 2 HCl

Phosphinous Amides R2 - P NR2

may be obtained by treating organophosphine halides with primary or secondary amines in ether or benzene at or below room temperature.

R2 PX + 2R'2 NH = R2 P NR'2 + R'2 NH.HX

An important amide is Dimethylamino Dimethylphosphine with the following reactions -

Me2 P-NMe2 +	H2O2	=	Me2 P (O) NMe2
	NH2Cl		Me2P (NMe2) (NH2)+ Cl-
	NH3		(Me2P)2 NH
	Me2 PH		Me2 P-P Me2
	S		Me2 P (S) NMe2
	HCl		Me2 PCl
	B2H6		Me2 P (NMe2) BH3
	ROH		Me2 P (OR)

Orthophosphate Esters are incredibly numerous and are found in many forms throughout our bodies. They are produced and used as plasticizers, flame retardents, reagents, solvents, pesticides, and nerve gases. They are classified as -

```
Monoesters        Diesters          Triesters
RO    O           RO    O           RO    O
  \  //             \  //             \  //
   P                 P                 P
  / \               / \               / \
HO   OH           RO   OH           RO   OR
```

As I have already stated, it is very hard to react alcohols directly with orthophosphoric acid. After 7 hours boiling together, there is very little yield. This process however can be speeded up dramatically by adding a condensing agent such as carbo-diimide (cyanamide) HN:C:NH or N:CNH2.

You can also condense the corresponding phosphite to yield the ester as we have already described. They can also be produced by adding water to the appropriate halophosphate (hydrolysis) -

$$(RO)\,POX_2 + 2H_2O \;=\; (RO)\,P\,(O)\,(OH)_2$$
$$(RO)_2\,POX + H_2O \qquad (RO)_2\,P\,(O)\,OH$$

Phosphorus Pentoxide is reacted directly with alcohol to yield a mix of esters -

$$P_2O_5 + 3\,ROH \;=\; 2\,(RO)\,PO\,(OH)_2 + 2\,(RO)_2\,PO\,(OH)$$

Phosphorus oxychloride reacts with phenols to yield triaryl phosphates.

$$3\,PhOH + POCl_3 = (PhO)_3\,PO + 3\,HCl$$

Triethyl phosphate is made by heating phosphorus pentoxide with diethyl ether in an ethylene atmosphere at 180 C.

$$P_2\,O_5 + 3\,Et_2\,O\ (\text{in } C_2H_4) = 2\,(EtO)_3\,PO$$

Pyrophosphate esters are made by heating a phosphate triester with phosphorus pentoxide or thionyl chloride -

$$2\,(MeO)_3\,PO + SOCl_2 = (MeO)_2\,P\,(O)\,.\,O\,.\,P\,(OMe)_2 + SO_2 + 2\,MeCl$$

The tetraethyl analogue has been used as an insecticide and is distilled off at low pressure.

This was one of the first toxic pesticides used as an insecticide that was very dangerous to humans. Invented by Schrader, it was toxic at 1 PPM making it marginally useful as a nerve liquid that could kill if delivered as a mist.

Halophosphates are made by reacting a phosphorus oxyhalide with the correct amount of alcohol or phenol-

$$POX_3 + ROH \;=\; (RO)\,P\,(O)\,X_2 + HX$$
$$POX_3 + 2\,ROH \qquad (RO)_2\,POX \quad + 2HX$$

The next section will cover the production of the actual pesticide/nerve acting agents. These materials are used in agriculture as spray mists and as dusts which are finely ground minerals impregnated with the liquid organophosphate. Most of these materials are very toxic to mammals and their use as weapons was quickly developed after their discovery. Much of the early research was actually done on humans in the German concentration camps of WW2.

A comparison of the toxicity of several organophosphates are described in the LD50 mice.

TEPP	1 PPM
Paraoxon	3 "
Sulfotepp	5 "
Parathion	6 "
Dimefox	7 "
Guthion	15 "
Phosphamidon	17 "
Fonophos	17 "
Schraden	20 "
Systox (Dimeton)	30 "
Methyl Parathion	30 "
Diazinon	100"
Bromophos	100"
Ethion	200
Phosmet	230
Dipterex	600
Malathion	1,500

The toxicity of less than 10 PPM of pure material means that a coffee cup thrown on an individual containing pure product will likely kill the recipient and possibly the paramedics that would come to the rescue as well.

Amidohalophosphates

```
R - N    O
     \  //
      P
     / \
R - N    X
```

All the chemicals produced in this group are very toxic. When X is fluorine, all the compounds are extremely toxic and a single exposure to a whiff of gas on a scratch can kill. One of the most toxic is -

```
(CH3)2 - N      O
          \   //
            P
          /   \
(CH3)2 - N      F
```

These are prepared similarly to Tabun described previously with a second stepwise reaction of the alcohol amine followed by reaction with Hydrofluoric acid or sodium fluoride.

Dimefox, the formula described above can also be made by reacting dimethylamine and potassium fluoride with phosphorous oxychloride as described in the Pesticide manual 4th Edition page 196 (Nov 1974)

Mipafox, also called a phosphinofluoridate, is produced by adding phosphorus oxychloride to chloroform and then reacting isopropylamine. This was further reacted with potassium fluoride as described in US Patent # 2,678,334, May 11, 1954 assigned to Pest Control Ltd.

V Series Nerve Agents

```
   R        O
     \     //
       P
     /   \
R - O     S - X
```

In this group, the R is the alcohol, but the X is a molecule which physically resembles cholinesterase. In the case of VX -

```
      CH3       O
          \    //
            P
          /   \
C2H5 - O      S - CH2CH2N [CH(CH3)2]2 - O - C2H5
```

In the case of its analogs with similar properties, the end portion following the S - CH2CH2N can be simple alcohols like (CH3)2 or (CH3)3, or complex as shown above where organic string is mixed and can end in C2H5 or other alcohol. The (CH3)3 is a quarternary ammonium compound derived by a reaction with methyl iodide which will be described shortly.

The base material for V gases is -

Triethyl Phosphite

```
C2H5 - O
          \
            P
          /   \
C2H5 - O      O - C2H5
```

323 grams of triethyl phosphite is added to 284 grams (126 ml) of methyl iodide. These are refluxed together for three hours and purified with distillation according to the procedure described in Organic Synthesis Volume 31 or Collective Volume 4, page 325.

This produces Diethyl Methyl Phosphonate

```
C2H5 - O       O
          \    //
            P
          /   \
C2H5 - O      CH3
```

Isomerization, Oxidation, and Dehydrohalogenation Weapons

There are a number of processes in which pesticides already available on the shelf, and military nerve agents already produced, may be made much more deadly and therefore much more useful as weapons. These processes I will describe in this book (some will not be revealed in this book) are -

1. **Isomerization** (and/or **transalkylation**) which involves the rotation of a double bonded atom with a different single bonded atom. This often results in increases of toxicity of 10 to 10,000 times. This is usually accomplished by heating, by storing at elevated temperatures in different solvents, and by exposure to direct sunlight or ultraviolet radiation.

2. **Oxidation** which allows the "thiono sulfur, mercapto sulfur, and phosphoroamides" substituents to substitute oxygen in place of sulfur and to add a double bonded oxygen to a nitrogen in the amides. These changes can also drastically increase toxicity of the parent organophosphate. This is accomplished by the adding of chemical oxidation agents or by photo induced oxidation.

3. **Dehydrohalogenation** is accomplished by treating organophosphate solutions in alkali which removes a halogen in the formula and alters the parents physical properties. Many of these make the original nerve acting agent much more toxic.

Isomerization

Early research into organophosphates would often produce some surprising and inconsistent results. A team of researchers would produce what they believed to be a very safe insecticide only to find out that when they stored it in an alcohol, or allowed it to stand in hot temperatures, it became much more deadly to the handlers who were to use it in the fields. What had taken place in the storage conditions is a process that is now known as "isomerization". This process would lead to the development of some incredibly deadly and fast acting nerve agents (whose formulas are classified top secret even today) that would kill nearly instantly at doses of less than 1 part per billion. The reports of Afghanistan soldiers dying instantly, frozen in position holding their rifles are easily understood when these deadly new compounds are accounted for.

Most of these super deadly formulations have at least one drawback (or advantage if you are on the receiving end). As their ability to kill goes up, so does their hydrolizability. This means that they easily take up moisture into their chemical formulas and quickly change into non or mildly toxic materials very quickly. That means that they do not persist very long in the environment and it is sometimes safe to pass through a treated area in as little as 10-30 minutes.

It is possible to isomerize 90% of Malathion by heating it at 150 C for 24 hours although this end material contains a mixture of several possible isomers. This combined with a malathionase binding phosphate like EPN or Dipterex will bring malathions toxicity close to that of many of the weaker nerve gases.

Parathion isomerizes to about 50% on heating at 140-180 C for 5 hours. Methyl Parathion yields about 83% in 5 hours at the same temperatures, or if mixed in ethanolic solution it will yield 35% in 4 hours at 100 C. If left standing in an ethanol solution for 5 months at room temperature, it will yield substantial isomerization. If exposed to ultraviolet light for 72 hours it will isomerize to a small extent (1.2%). Parathion however isomerizes readily and substantially if exposed to ultraviolet and sun light and as a result becomes much more toxic. This also yields a mix of at least 7 different isomers.

Heating time and temperature is an important part of the isomerization methods. The isopropyl analog of parathion in pure crystal form yielded isomers at 150 C in 6 hours but shows no isomerization at 110 C.

The solvent that an organophosphate is mixed into can enhance or decrease isomerization.

Solvent	Temp C	Isomerization at 39 days
Ethanol	37.2	56 %
Chloroform	37.2	23.5
Methyl ethyl Ketone	37.2	8.6
Dioxane	37.2	4.8
Ethyl Acetate	37.2	4.3
Benzene	37.2	4.1
2,2,4-Trimethylpentane	37.2	1.8
None	37.2	6.0

The above chart shows the isomerization of "Systox" after storage for 39 days at 37.2 C. It is obvious that if you are trying to make a safer pesticide that does not easily isomerize to large amounts of a more dangerous mix then you would choose 2,2,4-Trimethylpentane as a solvent for storage. If you are trying to make potential weapons of the parent systox compound, then you would mix and store it in ethanol at elevated temperatures.

As a general operating rule

1. polar solvents markedly increase the isomerization rates while apolar solvents usually decrease it.
2. Exposure to high heat (below decomposition) and increased duration increases isomerization.
3. Exposure to direct sunlight and/or ultraviolet light often increases isomerization.
4. Most isomerization substantially increases nerve acting properties of the phosphate.

A second type of isomerization can take place in organophosphates. this type is called "**Cis-Trans Isomerism**". When you look at an organophosphate, if there is a double bond present in the R, or X components formula, then it is possible for different substituents to switch positions. This is provided that the atoms are not the same and the double bond is not part of a ring structure.

```
Trans Isomer                Cis Isomer

X - CH                      CH - X
    \\                       \\
      CH - Y                   CH - Y
```

These types of bonds and structures occur in -

```
Phosdrin                              Phosphamidon

CH3 - O      O                        CH3 - O      O
         \  //                                 \  //
          P                                     P
         / \                                   / \
CH3 - O     C = CH - COOCH3           CH3 - O     COON (C2H5)2
             \                                     \
              CH3                                   CH3
```

The Phosdrin in the Thiono form was isomerized by about 50% in a carbon tetrachloride solution that was exposed to ultraviolet light for 30 hours.

One final comment is that once the isomers are produced into more deadly forms, they usually rapidly hydrolyze on exposure to moisture and humidity making them less potent very quickly.

Transalkylation

is a phenomena observed in "Systox" type organophosphates in which the compound splits apart forming two separate organophosphates that "self alkylate" into deadlier forms. A 1% solution of methyl systox, stored for 1 day at 35 C changed to where its LD50 for the rat fell from 60 PPM to 2 PPM making it 30 times more deadly. An impure solution of the thiono isomer changed in 1 hour at 37 C reducing the rat LD50 from 220 to 2 PPM making it 110 times as deadly.

The starting type of systox formulas usually are -

2X [(RO)2 P (O) S CH2CH2S C2H5 + H2O >

This transalkylation yields two new compounds -

(HO) (RO) P S - CH2 SCH2 C2H5

and (RO)2 P (O) S CH2 CH2 S+ C2H5 + OH
\
R

In this last formula, when R is a methyl group, the toxicity to the rat is increased about 1,000 times making it as deadly as many of the original nerve gas weapons. These types of reactions occur in stored samples and in aqueous solutions along with the expected hydrolysis. This transalkylation occurs faster when R = CH3 and is slower when R = C2H5.

The systox compounds, their formulas and toxicity are given in the following chart -

Compound	LD50 Rat in PPM
(CH3 O)2 P (O) SCH2 CH2 SC2H5	63-65
(CH3 O)2 P (O) S CH2 CH2 SC2H5 \\ O	47-65
O \\ (CH3 O)2 P (O) S CH2 CH2 S C2H5 / O	22-32
C2 H5 / (CH3 O)2 P (O) S CH2 CH2 S+ \\ CH3	.06-10
C2H5 / (C2H5 O)2 P (O) S CH2 CH2 S+ \\ CH3	.016-20
C2H5 / (C2H5 O)2 P (O) S CH2 CH2 S+ - C2H5	.010

Oxidation

Three substituents in organophosphates may be readily oxidized. These are "thiono sulfur, mercapto sulfur, and phosphoramides". These oxidation's usually will form a sulfoxide, sulfone, or a phosphate out of a thiophosphate.

Oxidation of (RO)2 P (S) X yields (RO)2 P (O) X

```
Sulfur Oxidation yields      Sulfoxide        Sulfone
                                                  O
                                                 /
                                -S-             -S-
                                  \             /
                                   O           O
```

The herbicides Co-ral, Ronnel, and Malathion have been oxidized in chloroform solution using Peracetic acid. Malathion and Ronnel have been oxidized using concentrated nitric acid. Bromine water has been used to oxidize many phosphorothionates and is useful if the end material is to be used as a deliverable weapon soon afterwards.

The oxidation of mercapto sulfur in Systox can be accomplished simply by mixing with hydrogen peroxide to yield the sulfoxide, or with potassium permanganate to yield the sulfone. Thimet can be oxidized to either form by controlled addition of monoperphthalic, peracetic, or perbenzoic acid. Some of these reactions occur in nature on the leaves of treated plants and workers who brushed the leaves have been poisoned by the tiny amounts that soaked into their shirts and through their skin.

Phosphoroamidates yield several oxidation products from permanganates, some of which are 10,000 times as toxic as Schraden (as deadly as Sarin), and some which are poor cholinesterase inhibitors.

An example of one of these oxidation's is -

```
          CH3                 CH3
         /                   /
    P - N            to  P - NH
         \
          CH2 OH                 + Formaldehyde  CH2 O
```

These types of isomerizations are catalyzed by addition of acid, or alkali, and/or heat. Other oxidizers that have been used include sodium hypochlorite, potassium dichromate, and various permanganate, peroxide, and peracetic salts and acids. Most of the oxidized materials are more toxic than their parent compounds and in some cases approach military nerve gases in activity.

Dehydrohalogenation

In the early research on the organophosphate "Dipterex", it was found that treatment with alkali produced a highly toxic, oily, and volatile (gas generating) impurity that separated out and would easily kill workers handling the material. The end material was DDVP which has since been incorporated into some insecticides itself. The process was dehydrochlorination in which a chlorine is reacted off in the form a hydrochloride leaving a new material with different properties from the parent compound.

The process was pH dependent with very little change occurring at a pH of 5.4 but 60% complete in 2 hours at pH of 8. In aqueous and solvent solutions, caustic soda, ammonia, and other strong alkalis work to effect this conversion at high pH. In anhydrous solutions, pyridine and triethylamine are the alkali's of choice.

In all formulas, the halogen (fluorine, chlorine, bromine, etc.) are removed and a new compound is created. In the case of less toxic starting materials the end product is often much more toxic. In the case of very toxic compounds, the end material may have less toxic properties.

Exposure to Light

By exposing organophosphates to visible and ultraviolet light, more toxic and more polar materials are nearly always produced. Most of these are much more toxic. This is due to isomerization, photo oxidation, and other processes which are not all fully understood.

A study of Parathion irradiation yielded the following characteristics.

As radiation time increased

1. There was a significant increase in anticholinesterase activity

2. A decrease in toxicity to the house fly

3. A decrease in assayable nitro-aromatic compounds (converted to other materials)

4. A decrease in the ability to lower blood cholinesterase of rats in feeding trials

The conclusions were that the irradiation produced a mix of parathion, paraoxon, other oxidation and degradation products, and isomers.

The conversion of P=S bonds to P=O bonds by any of the described methods always leads to increased toxicity.

Special Toxic Enhancing Ideas

In organophosphates that have phenyl groups, it has been found that by substituting *m*-dimethylamino or *m*-tertiary butyl derivatives, it was found that the cholinesterase inhibiting ability of these compounds increased 1,000 fold over the parent.

Early on it was theorized that cholinesterase may be bound on more than one site and efforts were made to find organophosphates that would bind on multiple sites and would therefore be more effective inhibitors, and be more effective weapons. Sarin, Soman, EPN, and some of the carbon isomers in Butonate, Dibrom, Dipterex, and Malathion were modified through the methods already described until special isomers were found that would make effective weapons. This author is aware of the publication of only one formula, a phosphonate, the *l* isomer being 10-20 times as deadly as the parent

$$(EtO)\ (Et)\ P\ (O)\ S\ CH_2\ CH_2\ S\ Et$$

In early research, it was discovered that some of the dangerous insecticides that were very toxic to people were poor cholinesterase inhibitors in the lab. It was soon discovered that all the phosphorothionates and many of the phosphoramidates are poisonous to people only because our liver converts them to deadly anticholinesterases. This accounts for delays in poisoning symptoms with these types of organophosphates.

In other research, it has been found that when certain organophosphates are combined, they are much more deadly than when used alone. The case of malathion and EPN was discovered in the 1950's when both mixed together yielded LD50's of 40-50 times their own toxicity. This was due to the tying up of the malathionase enzyme in humans. This potentiation was observed in other chemicals when DDT and piperonyl butoxide enhanced the effects of each other.

Those chemicals that have been reported to be drastically synergistic, making them potential nerve based weapons are -

Malathion	+	EPN
		Dipterex
		TOCP
	partially by	Thimet, Systox, Phosdrin, Diazinon, Methyl Parathion, and Parathion

This was evidently due to the second phosphate interrupting the livers ability to degrade malathion and remove it from the body.

When phosphorothionates are oxidized (from bromine oxidation) and then included in the delivery system with malathion, all of them show greatly increased inhibition of malathionase.

Antidotes and Defenses

Protection against nerve agents usually involves creating physical barriers against exposure to the chemicals and reacting them to less toxic forms with moisture and chemicals. Full body protective suits in combination with gas masks or scuba gear prevent contact with skin surfaces or breathing in the agent. Washing off the suits in a shower before taking them off reduces potential exposure from residues.

For ordinary citizens, the only available protection is usually a gas mask. This can be supplemented with a number of field improvised protections.

* Vaseline can be used to provide a barrier against liquid and gas agents (but not the dust). Mixing diatomaceous earth with the vaseline will provide a highly reactive silica source for detoxifying Sarin and other phosphonofluoridate weapons. Many other nerve agents can be reacted out by adding various chlorine compounds such as the swimming pool hypochlorite granules on separate layers outside the vaseline or clothing. The chlorine reacts with most nerve agents. Care must be taken to make sure that it is not applied into the layer next to the skin because it causes skin burns.

* Using the gas mask filter in combination with a fan to produce a positive flow filtered air environment in a room or the inside of a car. A fan draws air into the vehicle through the mask filter which reacts out the nerve agent. The clean air the pushes out and displaces the air in the vehicle through the cracks and crevices. This prevents the toxic gas from seeping into your protected environment.

Antidotes developed and tested for protection against nerve agents first included atropine which was very effective against phosphonofluoridates like Sarin but much less effective against other classes of nerve agents. It usually increased the LD 50 to Sarin about 1,000 times in monkeys while only improving it about 50 times when the herbicide paraoxon was used.

When rabbits were tested against DFP vapors in 1946, it was discovered that it killed 83% of the control animals. When atropine (10 mg/kg) was given alone, it reduced the death rate to 53%, and when given immediately after exposure in combination with 400 mg/kg of magnesium sulfate it reduced the death rate to 13%.

Various respiratory stimulants have also been tested and many showed modest improvements in protecting against nerve agents.

While atropine acts primarily as a blocking agent, there have been several compounds developed as reversing agents that are much more effective than atropine. The most widely reported beginning in 1956 is 2-PAM (Pyridine-2-aldoxime methiodide). When used alone, its effects on the nerve agent are small. When used in combination with atropine which acts as a potentiator, it was found to give complete protection against 10 times the LD50 of Paraoxon in mice. The atropine was administered 30 minutes before exposure while the 2-PAM was administered 1-2 minutes after exposure. Results varied with the nerve agent involved. The combination only raised the LD50 to Sarin by 2 times while with TEPP it raised it 32 times and with Paraoxon by 128 times.

Recovery in medical patients exposed to dangerous doses of Parathion herbicide in hospitals has been reported to be rapid with relief from pain and muscle effects taking place within minutes.

Various chemical defense groups have produced improved oximes and hydroamic acids which effectively lower toxicity of the nerve agents but are themselves toxic.

Detailed studies show that many of these compounds were specific at working in some organs and tissues, but not others in reactivating cholinesterase activity and many of the results have not been made public.

Authors Comments

I have recently been asked why I am writing a book which contains information of this type of potentially dangerous materials. There are many reasons which motivated me over time to complete this work.

1. The lawsuit and ultimate destruction of my feed and soybean businesses in the 1980's caused me lose any faith or hope in the lawyers and courts of this country. I briefly recounted what had happened in my introduction to volume 1.

2. The large phosphate companies had a hand in the destruction of my businesses. When we finally completed the phosphate plant in the late 1980's, we had fixed the laboratory and fluorine problems and were state approved, these large companies decided as a group that they would not let us join their fraternity of manufacturers and told me so in no uncertain terms. I would not be allowed to take their cheap raw materials like phosphoric acid or phosphate rock and defluorinate it with my new process so it could be used in making expensive feed grade phosphates.

They shut us off from all raw material supplies. Even with my offering to pay cash in advance, not a single manufacturer in the entire US would sell us phosphoric acid or phosphate rock, even though many advertised millions of tons for sale. Some snickered at me on the phone during my attempts to buy the raw materials. Others flat out told me that I would be driven out of business. Others wouldn't talk to me at all. My friends at TVA that helped me in solving the fluorine problem told me that what these companies were doing was illegal and that I should be able to sue (lawyers again). No lawyer would take the case on against such a large and unified trade on a contingency and our small size made it impossible to pay for a court battle. Once again, financial size rather than justice and fair play rules America. This episode ended any "Buy American" sentiment that I may have had in my heart. When Americans deliberately use their position and financial powers to enrich themselves and block out any possible competitors, and can get away with it, then their is no hope left in the American system. My writing the directions and knowledge of converting the phosphorus products of this entire industry into weapons is a sort of poetic justice. The obvious response of the government will be to remove the organophosphates from the shelves in the name of "protecting the public". The effect of this will likely cost the big phosphate companies many billions of dollars. Then it may be time to write directions for conversion of the fertilizer phosphates to VX analogs. That, I think would quickly end the idea of using government regulations to protect the public safety. It would be a practical impossibility.

3. The US government deliberately writes many laws to help the large companies accomplish the weeding out of ordinary Americans from the pretend equal opportunities that our constitution and bill of rights supposedly would guarantee for us. Patent laws are enacted to weed out most Americans from being able to own the rights to their own inventions unless they start out with great financial and psychological wherewithal. Money rather than merit determine whether you will receive a patent in America. This is why almost all patents are now owned by corporations. The laws were deliberately designed to weed most ordinary Americans out of the system. Only corporations and wealthy individuals are able to protect and perpetuate their empires while legally excluding everyone else from fairly competing with them.

This type of legislating is done at all levels and throughout all industries. Recently, I was traveling through Colorado and had a flat tire. The bolt holding on my spare had rusted in place and could not be removed. I hitched a ride to the nearest gas station. The owner of this station was an elderly man who for many years had towed stranded motorists into town.

While waiting, I visited with many of his customers and found that he had a reputation as a good Samaritan and would sometimes not even charge poor people for towing if they were obviously desperate. The state of Colorado sent inspectors to his station and in accordance with the laws they had passed, prevented him from offering towing services any longer by requiring him to spend thousand of dollars of extra equipment he was unable to afford.

The net effect is that only a couple of companies were in the towing business and only one of these was available to tow me in and change my tire. The price for a 20 mile tow and change of tire was $137.50 because of the monopoly that the government regulations had effectively given them solely on the basis of how much money they had to enter and control the business.

This effect is seen in every industry and every part of American life. The rules are being written to partition off all the fields of business in America creating a country where only rich people have equal opportunity amongst themselves and all other Americans become indentured servants or slaves to those with wealth and power.

3. A few days ago, I was traveling to a gun show and became stuck in a traffic jam in Chattanooga. They had funneled four lanes of traffic into one for major replacement of part of the interstate. It was hot and humid, I had no air conditioning, and my patience had reached its end so I became Darwinian in my thinking. I finally decided that if they ask me why I wrote this book I would tell them "to reduce traffic congestion". You see, I can still use humor to fight back.

In the end, Washington and all the state governments need to know that they cannot simply write laws and expect to control and regulate all of the people and their lives. The people can in fact, finally refuse to obey and live by their rules any longer. The power of the government to send masked police, or even the army into peoples homes, has up to this point in time given them the power to impose their rules on everyone. Their is only one way to balance this power and that is to make sure that the citizens have such knowledge in their possession that the power of the police and the army effectively becomes irrelevant. On that day, this government will have to find new rules that are in fact just for everyone, not just the ones who fund their election campaigns.

The ability of the citizens of this country to have genuine science and knowledge in their corner for once, and not just in the governments corner, will, in the end, shift the balance of power in this nation. The people in Washington will learn that it is the conscience of its citizens and not the threat of punishment or loss of life that will govern whether its laws will be obeyed. This will depend on the justness of both the character and the enforcement of these laws. The rights of the constitution and the promise of genuine, equal, opportunity in this country will no longer be worthless words on a piece of paper. The citizens will have the power to back up their demands for justice and fair play. That is why I wrote this book!